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Brief overview on cellulose dissolution/regeneration interactions and mechanisms

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ABSTRACT

The development of cellulose dissolution/regeneration strategies constitutes an increasingly active research field. These are fundamental aspects of many production processes and applications. A wide variety of suitable solvents for cellulose is already available. Nevertheless, most solvent systems have important limitations, and there is an intense activity in both industrial and academic research aiming to optimize existing solvents and develop new ones. Cellulose solvents are of highly different nature giving great challenges in the understanding of the subtle balance between the different interactions. Here, we briefly review the cellulose dissolution and regeneration mechanisms for some selected solvents. Insolubility is often attributed to strong intermolecular hydrogen bonding between cellulose molecules. However, recent work rather emphasizes the role of cellulose charge and the concomitant ion entropy effects, as well as hydrophobic interactions.

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1. Cellulose generalities

Cellulose is a readily available and renewable biopolymer abundantly found in nature, typically combined with lignin and hemicelluloses in the cell wall of upper parts of plants [1]. This homopolysaccharide is formed by linearly connecting D-glucose units condensed through $\beta(1-4)$ glycosidic bonds (Fig. 1). The degree of polymerization (DP) can vary considerably depending on the source (i.e., DP from 100 up to 20000) [2]. From the single anhydroglucopyranose unit, AGU, up to the micro and macro fibrils, cellulose organizes in a rather complex fashion where an extended intra- and intermolecular network of hydrogen bonds is indicated as the basis of cohesion between cellulose molecules (Fig. 1). It is believed that intramolecular hydrogen bonds provide

chain stiffness, while, on the other hand, intermolecular hydrogen bonds allow the linear polymer molecules to assemble in sheet-like structures [3]. A more recent perspective highlights the amphiphilic nature of cellulose (Fig. 2) [4–6]; the equatorial direction of a glucopyranose ring has a hydrophilic character because all three hydroxyl groups are located on the equatorial positions of the ring. On the other hand, the axial direction of the ring is hydrophobic since the hydrogen atoms of C–H bonds are located on the axial positions of the ring. Thus, cellulose molecules have an intrinsic structural anisotropy where the rather flat ribbons present sides with clear differences in polarity [7–9]. Such structural anisotropy is expected to considerably influence both the microscopic and macroscopic properties of cellulose but has largely been neglected in most discussions.

Cellulose can be considered as a semi-crystalline polymer with amorphous regions, of low order, coexisting with higher order crystalline domains [10]. The origin and pretreatments of a cellulose sample

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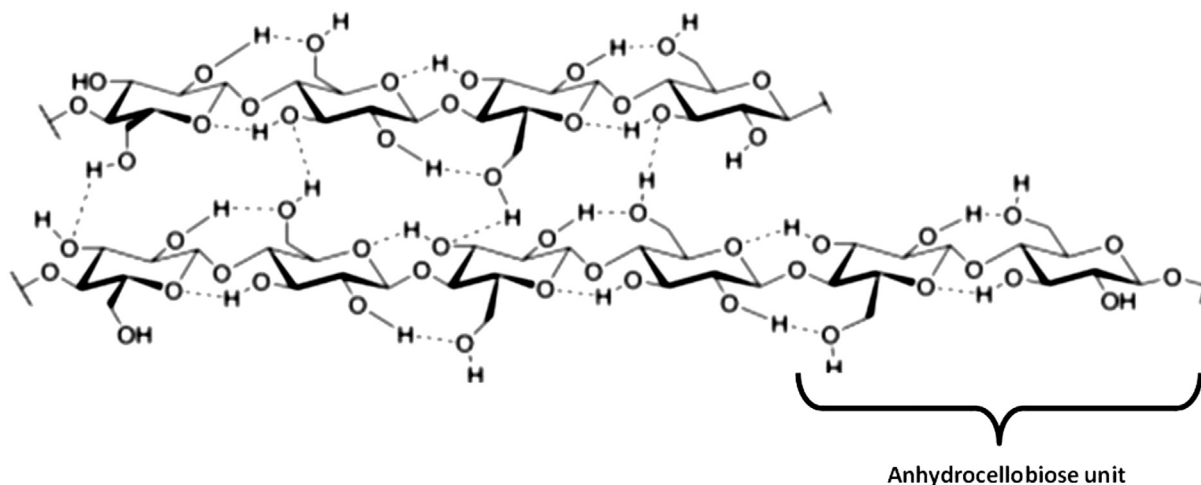


Fig. 1. Molecular structure of cellulose where the extended network of intra and inter-hydrogen bonding is represented. The anhydrocellobiose unit (i.e., disaccharide of two glucose molecules) is highlighted.

determines the degree of crystallinity of cellulose, which typically is found between 40% and 60%. Several suggestions on how these crystalline and non-crystalline regions are intermixed have been developed over the years, such as single crystals or uniform elementary fibrils, but nowadays, the so-called “fringed fibrillar model” is widely accepted [11–16]. In this model, the cellulose nanofibril is not regarded a single crystal but rather as a less structured arrangement of non-uniform crystalline segments accompanied by amorphous parts, both longitudinally and laterally displaced [12].

Apart from being used in unmodified forms, such as wood or cotton, cellulose can be extracted from its natural sources and either used in the paper industry or, in a smaller scale, in some specific applications such as regenerated fibers (e.g., Lyocell or viscose). In fact, it is believed that forest-based raw materials, such as cellulose, can play a major role in replacing fossil oil-based fibers and cotton by new ecological man-made fibers in both woven and non-woven end applications. The success of this replacement is intimately dependent on the development of new solvents and strategies for dissolution and regeneration. Cellulose may also be modified by chemical, enzymatic or microbiological methods to obtain new valuable derivatives and materials. Large-scale production of cellulose derivatives (mainly ethers and esters) and regenerated materials (i.e., fibers, films, food casing, membranes, and sponges, among others) find applications in several important commercial areas such as the membrane, polymer and paint industries [3].

A challenging issue is the fact that many important applications of cellulose involve its dissolution. Due to the complexity of such a biopolymeric network, the partially crystalline structure and the extended non-covalent interactions among molecules, chemical processing of

cellulose is rather difficult. Cellulose does not melt nor is it soluble in common aqueous and organic solvents [2,17]. However, this polysaccharide is soluble in more exotic media with no apparent common properties [18]. The more consensual vision among leaders in the field has been that the key to dissolve cellulose resides in the solvent capacity to break the above mentioned intra- and intermolecular hydrogen bond network [19]. Other interactions among cellulose molecules have been mostly ignored. Recently, we have reanalyzed this problem and argued against this accepted picture [4–6]. Instead, we have concluded that cellulose has clear amphiphilic properties and a careful examination of the interactions involved suggests that hydrophobic interactions play a significant role in governing cellulose solubility.

2. Solvents used in cellulose dissolution

Why is cellulose dissolution so important? The following reasons can be enumerated: preparation of regenerated and innovative materials such as fibers (e.g., textile applications) and films (e.g., packaging applications), production of valuable cellulose derivatives in a homogeneous environment (note that typical solvents cannot penetrate inside crystalline regions of cellulose and heterogeneous modification is restricted only to the surface of the crystallites), and finally, to degrade cellulose more efficiently (e.g., important for, for instance, biorefinery purposes).

Typically, cellulose dissolution is preceded by polymer swelling, which is defined as a process where the solvent molecules penetrate and labilize the cellulose structure to a certain extent, leaving the volume and physical properties of the biopolymer significantly altered

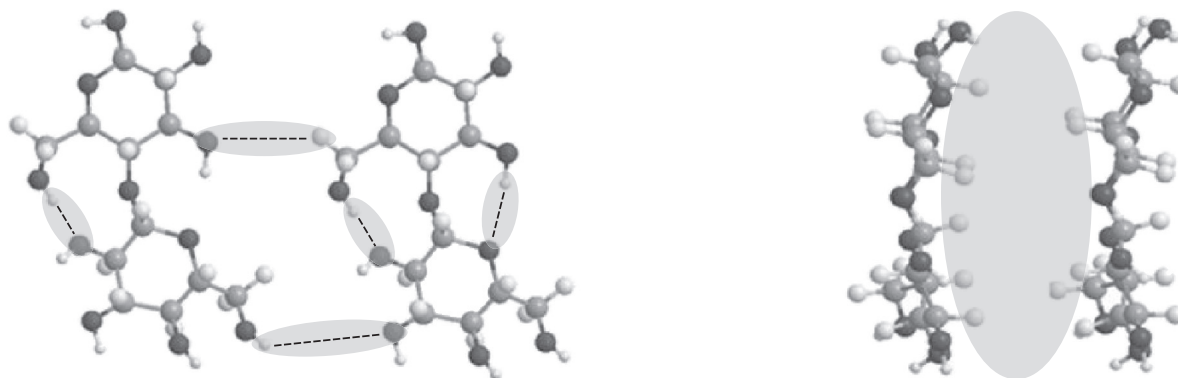


Fig. 2. Hydrophilic and hydrophobic parts of the cellulose molecule: left, top view of the glucopyranose ring plane highlighting hypothetical hydrogen bonding between the hydroxyl groups located on the equatorial positions of the intermediate ring; right, side view of the glucopyranose ring plane showing the hydrogen atoms of C–H bonds on the axial positions of the ring.

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