



Competing forces during cellulose dissolution: From solvents to mechanisms



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ABSTRACT

Cellulose is a polymer so widely abundant and versatile that we can find it almost everywhere in many different forms and applications. Cellulose dissolution is a key aspect of many processes; the present treatise reviews the main achievements in the dissolution area. In particular, the main solvents used and underlying mechanisms are discussed. As is described, cellulose solvents are of highly different nature giving great challenges in the understanding and analyzing the subtle balance between different interactions. Recent work has much emphasized the role of cellulose charge and the concomitant ion entropy effects, as well as hydrophobic interactions.

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1. Cellulose: a background to structural and solubility aspects

The scientific cellulose story starts with the French chemist Payen [1] who isolated it from green plants and reported its elemental composition in 1842 [2]. Cellulose is a linear homopolymer composed of D-anhydroglucopyranose units (AGU), which are connected by $\beta(1-4)$ -glycosidic bonds (Fig. 1a) [3].

The size of the cellulose molecules can be defined by the average degree of polymerization (DP). The average molecular weight is estimated from the product of the DP and the molecular mass of a single AGU. Each AGU bears three hydroxyl groups (one primary and two secondary moieties that represent more than 30% by weight), with the exception of the terminal ones. This makes cellulose surface chemistry quite intriguing and opens a broad spectrum of potential reactions, which typically occur in the primary and secondary alcohols [4••].

This readily available and renewable biopolymer is abundantly found in nature, typically combined with lignin and hemicelluloses in the cell wall of the upper parts of plants. From the single AGU up to the micro and macro fibrils, cellulose organizes in a rather dense and highly hierarchal fashion where an extended intra- and intermolecular network of hydrogen bonds is believed to constitute the basis of cohesion between cellulose molecules [5•]. A more recent perspective highlights the amphiphilic nature of cellulose (Fig. 1b) [6•,7••]; 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 and due to intra- and intermolecular hydrogen bonding, there is a formation of rather flat ribbons, with sides that differ markedly in their polarity [8•,9•,10•]; this is expected to considerably influence both the microscopic (e.g. interactions) and macroscopic (e.g. solubility) properties of cellulose.

As expected for a semi-crystalline polymer, cellulose can adopt several forms in the cell wall of a plant; amorphous regions (low order), are found to coexist with crystalline domains (high order) [11•]. The degree of crystallinity of cellulose, usually in the range of 40–60%, depends on the origin and pretreatment of the sample [5•]. Interestingly, the parallel arrangement found in nature (so called cellulose I), is not the most stable structure for a cellulose crystal; when dissolved and recrystallized, cellulose chains can adopt an anti-parallel arrangement known as cellulose II type crystal [12,13]. This intriguing process is still not understood in detail. It has been postulated that the transition from cellulose I to cellulose II crystals requires only a translational movement of molecules [11•].

Apart from being used in unmodified forms, such as wood or cotton, cellulose can be extracted from its natural sources and then either used for the paper industry and, in a smaller scale, for some specific applications such as regenerated fibers (Lyocell or Viscose). Cellulose may also be modified by chemical, enzymatic or microbiological methods to obtain new derivatives and materials. Large scale production of cellulose derivatives (mainly ethers and esters) and regenerated materials

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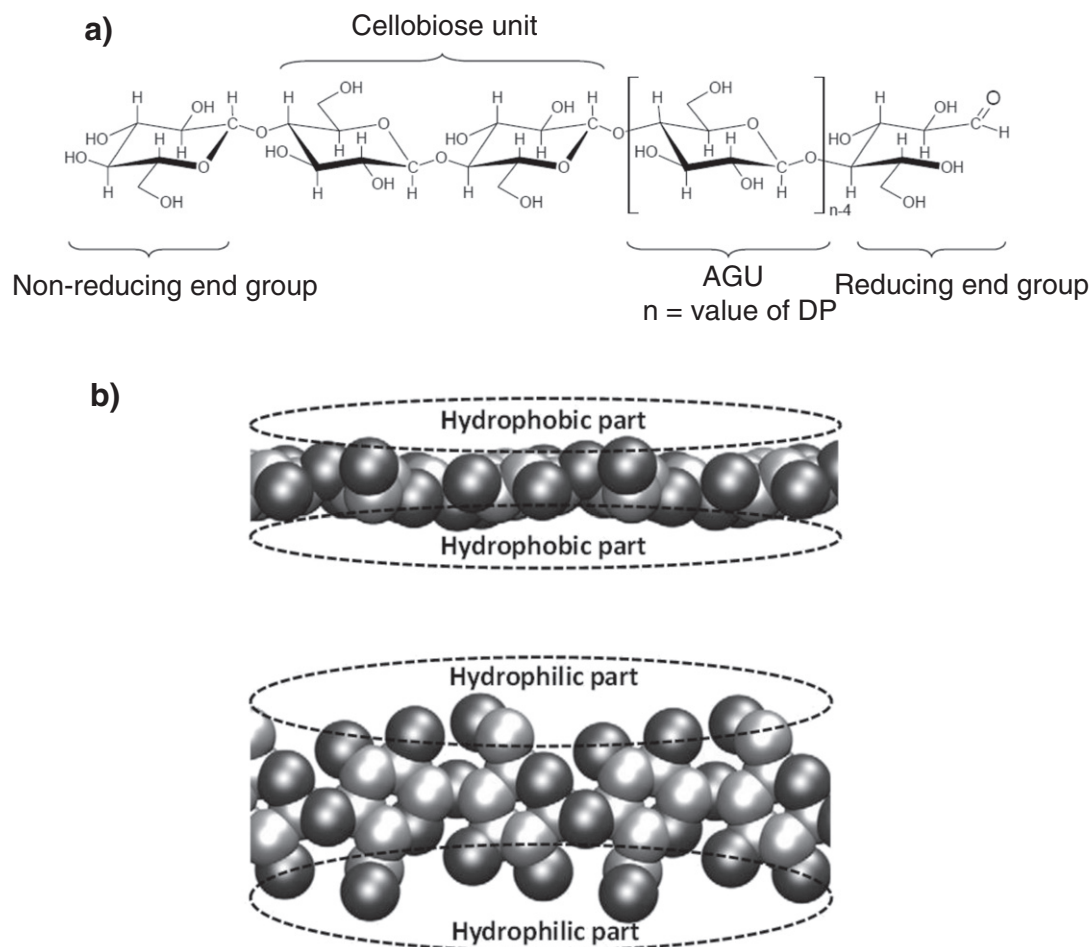


Fig. 1. a) Molecular structure of cellulose (Adapted from reference [11]) and b) a van der Waals surface representation of the cellulose chain, seen from 'above' and from the side, with oxygen atoms colored black and the non-polar carbon atoms shaded gray. The hydrophobic and hydrophilic areas are highlighted by the dashed ellipses. Note that the aliphatic protons are all in axial positions pointing perpendicular to the ring but, for clarity reasons, they are not shown in this representation (Adapted from reference [17]).

(i.e. fibers, films, food casing, membranes, and sponges, among others) finds applications in several important commercial areas such as the membrane, polymer and paint industries [5[•]].

On the other hand, many important applications of cellulose involve its dissolution and normally this is a challenging step.

Due to the complexity of such a biopolymeric network, the partial crystalline structure and the extended noncovalent interactions among molecules, chemical processing of cellulose is rather difficult. Cellulose is neither meltable nor soluble in usual solvents; water and typical organic solvents fail in this respect [3,14]. However, this biopolymer is soluble in more exotic media with no apparent common properties [15[•]]. This will be thoroughly discussed in this treatise.

Despite many and scattered opinions, 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 [16]. Other interactions among cellulose molecules have largely been neglected. We have recently analyzed the problem and argued against this accepted picture [6[•],7^{••}]. 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. In fact, hydrophobic interactions have been shown to markedly contribute to the crystal-like structure of cellulose and its stability over a hypothetical solution state; from free energy simulations in oligomers it has been estimated that there is a 2.0 kcal/mol/residue contribution for

the hydrophobic stacking while the estimated hydrogen bonding contribution is about eight times less [17^{••}].

2. Cellulose swelling and dissolution: macroscopic aspects

From a thermodynamic point of view the dissolution of a polymer, such as cellulose, in a solvent is, of course, governed by the free energy of mixing [18]. A negative value of the free energy change on mixing means that the mixing process will occur spontaneously. Otherwise, two or more phases may result from the mixing process. The higher the molecular weight, the weaker is the entropic driving force contribution for dissolution [19]. Under these conditions, the enthalpy term will be the crucial factor in determining the sign of the Gibbs free energy change. However, polymer dissolution is typically controlled by kinetics rather than thermodynamics and cellulose is, as we will see, a very clear example of this. A reasonable solvent for cellulose dissolution must be able to overcome the low entropy gain by favorable solvent/polymer interactions. Since in our view cellulose should be regarded as an amphiphilic molecule, we believe that research aiming in creating a basis for the development of new solvents should focus, not only in eliminating hydrogen bonding but also, more importantly, on eliminating hydrophobic interactions.

Cellulose swelling normally precedes dissolution. In this process, the solvent induces changes in the molecular order of the native polymer by overcoming to a variable extent the intermolecular interactions among

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