The Subtleties of Dissolution and Regeneration of Cellulose: Breaking and Making Hydrogen Bonds

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Cellulose dissolution and regeneration are old topics that have recently gained renewed attention. This is reflected in both applications - earlier and novel - and in scientific controversies. There is a current discussion in the literature on the balance between hydrogen bonding and hydrophobic interactions in controlling the solution behavior of cellulose. Some of the key ideas are recalled.

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Challenges and Opportunities

It is evident that today's society is placing an increasing demand on materials, which, in turn, is leading to a "carbon shortage" in certain industries. Industries need to become more resource-conscious and make use of what already exists, namely using other renewable and sustainable resources. The agro-forestal and related industries can indeed raise many resource challenges for society and suppliers in the near future. In this context, it is thus predicable that cellulose, as a widely abundant and versatile biopolymer, will assume a leading role. Cellulose is found in many different forms and applications. However, in some of these applications, cellulose dissolution and regeneration are key (and challenging) aspects. Due to the complexity of the biopolymeric network as well as to the partially crystalline structure and extended noncovalent interactions among molecules, chemical processing of cellulose is rather difficult. A wide variety of suitable solvents for cellulose is already available (Medronho and Lindman 2014). 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. The problem of obtaining a picture of molecular processes is not trivial since cellulose solvents are of remarkably different nature, and thus the understanding of the subtle balance between the different interactions involved becomes non-trivial.

Thermodynamics and Kinetics

"Cellulose itself is insoluble in water due to the many and strong hydrogen bonds". This and other similar statements have been extensively repeated in specialized literature. Furthermore, it is typically argued that "the key to the solution of this problem of cellulose solubility is to search for a solvent that can destroy effectively the interchain hydrogen bonding in cellulose". It is unquestionable that in solid cellulose there are multiple hydrogen bonds between the molecules that need to be broken in order to achieve dissolution. However, cellulose molecules are not transferred from the solid state to a

situation in which there are no intermolecular interactions (vacuum). Rather, they are transferred into a medium in which cellulose molecules experience other intermolecular interactions of considerable strength. Taking water as solvent, in fact, the solvent-cellulose hydrogen bonds are found to be as strong as the cellulose-cellulose hydrogen bonds. Thus, it is reasonable to assume that other interactions must explain the insolubility of cellulose in water and/or in other solvents.

Generally, in any solvent, the solubility of polymers is low when compared to low molecular weight compounds. The solubility decreases with increasing molecular weight, due to the low translational entropy. For flexible polymers, in general, and for polyelectrolytes, in particular, the entropy loss is counteracted by configurational entropy and counterion entropy, respectively.

In a practical dissolution case, it is important to consider not only the solubility and concomitant interactions but also the kinetics of the process. This should not be neglected, because polymer dissolution is often controlled by kinetics rather than by thermodynamics. Polymer dissolution is typically a slow process, and it becomes yet slower when increasing the molecular weight of the polymer. This is mainly attributable to physical entanglement effects, which are more important for the rate of dissolution than specific intermolecular interactions. Over the years, different strategies have been developed to increase the rate of dissolution, such as the use of different chemical, mechanical, or even enzymatic pre-treatments.

Regeneration also Involves Breaking Hydrogen Bonds

For cellulose molecules in aqueous medium, there are strong water-cellulose hydrogen bonds, in fact of the same strength as the cellulose-cellulose hydrogen bonds. (In other solvents, the cellulose-solvent interactions may be of similar strength or slightly weaker.) Therefore, regeneration of cellulose from a solvent would face the same problem of breaking hydrogen bonds as on dissolution, but this is clearly not observed.

Questioning of Hydrogen-bond Mechanism

Recently, the "hydrogen bond mechanism" has been intensively discussed in the literature and has been challenged by general arguments regarding interactions, as well as by simulations and experimental studies (Glasser *et al.* 2012; Medronho *et al.* 2015). In addition, computer simulations are providing a deepened understanding (Bergenståhle *et al.* 2010).

From a general physico-chemical perspective, this focus on hydrogen-bonding is rather surprising, as the general teaching is that the dissolution of any solute (low or high molecular weight) in water is facilitated by hydrogen-bonding ability. Indeed this misunderstanding is not found in early literature of leaders in the field but seems to have arisen later. Partly it has arisen from misinterpretations of experimental findings (for instance, NMR studies) but amplified by the tendency of repeated citing of statements without going back critically to the original work.

Amphiphilicity and Charges Control the Dissolution and Regeneration of Cellulose

Recent work has re-examined the basis of cellulose solubility and argued that cellulose has both hydrophobic and hydrophilic segments, and thus should have significant amphiphilic properties (Lindman *et al.* 2010; Medronho *et al.* 2012). Looking into the

crystal structure of cellulose, it is inferred that indeed C-H and C-O bonds are distinctly segregated and therefore cellulose molecules have an intrinsic structural anisotropy (Biermann *et al.* 2001; Yamane *et al.* 2006; Diddens *et al.* 2008). Computer simulations have revealed that hydrophobic interactions contribute strongly to cellulose-cellulose attractions (Bergenstråhle *et al.* 2010). Additionally, for aqueous systems, addition of urea, well known for eliminating hydrophobic interactions in many situations, increases markedly the cellulose solubility (Cai and Zhang 2005; Bergenstråhle-Wohlert *et al.* 2012; Xiong *et al.* 2014; Wernersson *et al.* 2015). Furthermore, surfactant addition has been found to strongly reduce cellulose-cellulose association controlling the regeneration (Yan and Gao 2008; Medronho *et al.* 2015).

Because of the counterion entropy, ionic polymers have a much higher solubility in water than non-ionic ones. For cellulose, both protonation at low pH and deprotonation at high pH are well known to lead to dissolution. Strikingly, acids and bases with organic counterions are more powerful in dissolution than their inorganic counterparts, which again emphasizes the role of hydrophobic interactions (Abe *et al.* 2012).

Regarding nonaqueous solvents for cellulose, it is noted that they are typically asymmetric, displaying both polar and nonpolar properties. In several important solvents, such as the N-methylmorpholine-N-oxide (*cf.* Lyocell process) and ionic liquids, the amphiphilic character of the solvent is evident. In several other solvent systems the mechanisms are less clear and further research is needed to determine the crucial roles of the different interactions involved.

In summary, the dissolution and regenerative precipitation of cellulose appear to depend upon a subtle interplay of forces, among which hydrogen bonds are only one of the important factors and do not seem to be the most significant driving force. Key factors instead include hydrophobic interactions, due to the amphiphilic character of cellulose, as well as the entropy of the counterions for the case that cellulose molecules have a net charge; this net charge can arise from protonation or deprotonation as well as association with charged species.

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