

Understanding the Dissolution of Cellulose in Ionic Liquids via Molecular Dynamic Simulations

David Friday

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Cellulose (Figure 1) is one of the most abundant bio-polymers on earth, being produced naturally by plants at rate of 10^{12} tons per year.¹ It has excellent material properties (strength and stiffness) and high energy density making it a renewable candidate to replace petroleum-based products in several material and energetics applications. Furthermore, it is largely derived from CO_2 , making it a natural mechanism for carbon sequestration in efforts to reduce atmospheric CO_2 levels.

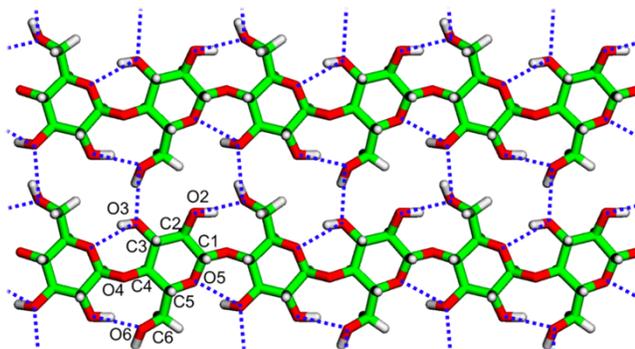


Figure 1. Cellulose $I\beta$ sheet with hydrogen bonds shown as dotted blue lines. Figure from Ref 2.

One of the greatest challenges to using cellulose on an industrial scale is its poor solubility in most solvents, making it difficult to process.² Cellulose is a polymerized carbohydrate having 3 alcohol groups per monomer, creating a strong network of hydrogen bonds between chains when in its natural crystalline form, making dissolution a challenge (See Figure 1). In 2002, Rodgers discovered that cellulose is soluble in 1-butyl-3-methylimidazolium chloride and a few other ionic liquids when heated to $100\text{ }^\circ\text{C}$.³ The following decade of research discovered a host of ionic liquids with variable solubility. What remained unclear is why certain ionic liquids, mostly imidazolium-based ionic liquids, paired with small counter anions (Figure 2), were such effective solvents. Specifically, what made cellulose soluble in these ionic liquids, and what are the mechanisms that enabled dissolution?



Figure 2. Common ionic liquids used to dissolve cellulose $I\beta$ bonds. Figure from Ref 2.

The first theoretical paper addressing this issue was a molecular dynamics study published in 2010, that focused on understanding the energetics of how 1-ethyl-3-methylimidazolium (EMIM^+ in Figure 2) acetate binds to cellulose in solution by calculating the ensemble averaged interaction energy of the anions, cations, and a single chain of cellulose.⁴ This study and others (including polarizable force fields)⁵ concluded that approximately 70% of the cellulose-ionic liquid binding energy comes from the anion (e.g. Cl^- , Ac^-) with its relatively localized charge forming strong electrostatic hydrogen bonds with cellulose. The imidazolium cation, with its more distributed charge, primarily positions itself on the aliphatic backbone of cellulose, engaging in van der Waals interactions, and ensuring charge neutrality in the polymer's local environment.⁶ Still, cation selection was found to be important in two ways. First, long alkyl side chains could interfere with the

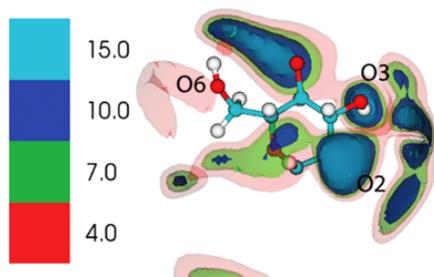


Figure 3. Chloride radial distribution function around a cellulose monomer dissolved in BMimCl . Figure from Ref 6

anion's access to cellulose hydrogen bonding sites, reducing overall interaction energy. And second, the electrostatic interactions between aromatic and allyl hydrogen atoms and ether oxygen atoms was found to be able to significantly enhance the cation's interaction energy, a fact observed experimentally by an over 20-fold increase in solubility from replacing a propyl side chain with an allyl side chain.⁷

Progressive gains in computational capabilities has allowed more recent work to investigate the large length and time scales (30 chains for 100s of nanoseconds) required to observe the mechanism of cellulose dissolving in several ionic liquids.² This work reveals that the mechanism of dissolution begins with the anions interfering with inter- and intra-chain hydrogen bonds across a sheet, followed by the cation stabilizing the broken hydrogen bonds, and incorporating itself between vertically stacked chains as it is lifted off the crystal into the solution (see Figure 3). These dynamics were further enhanced by the cellulose chain gaining access to a larger portion of conformational space (ie. skew-boat conformation and glycosidic bond rotations) due the disruption of intra-chain hydrogen bonding. Furthermore, this study found that the solubility of cellulose in the studied ionic liquids correlated best with the number of hydrogen bonds remaining at the end of the 250 ns simulation and not the total interaction energy. These findings confirm that the most effective ionic liquids are those that can interfere with the hydrogen bonds in cellulose and also provides a mechanism to possibly estimate the solubility of other ionic liquids via molecular dynamics simulations.

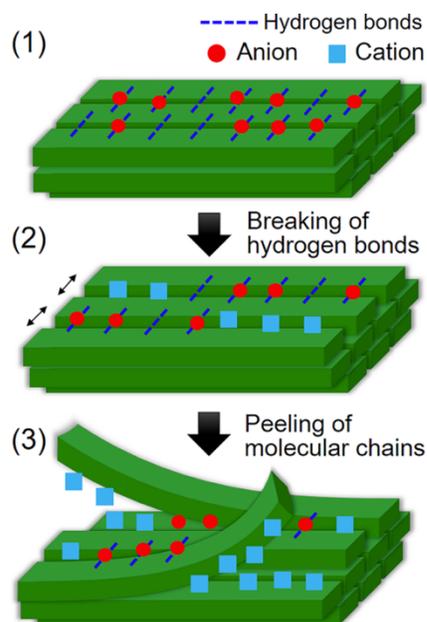


Figure 3. Cartoon of the cellulose dissolution mechanism. Figure from Ref 2.

References:

1. Huber, Tim, et al. A critical review of all-cellulose composites. *J. Mat. Sci.* **2012**, *47*, 3 1171-1186.
2. Uto, Takuya, Kazuya Yamamoto, and Jun-ichi Kadokawa. Cellulose crystal dissolution in imidazolium-based ionic liquids: A theoretical study. *J. Phys Chem. B* **2018**, *122*, 1 258-266.
3. Swatloski, Richard P., et al. Dissolution of cellulose with ionic liquids. *J. Am. Chem Soc.* **2002**, *124*, 184974-4975.
4. Liu, Hanbin, et al. Understanding the interactions of cellulose with ionic liquids: a molecular dynamics study. *J. Phys. Chem. B* **2010**, *114*, 12, 4293-4301.
5. Kan, Zigu, et al. Polarization effects on the cellulose dissolution in ionic liquids: Molecular dynamics simulations with polarization model and integrated tempering enhanced sampling method. *The Journal of Physical Chemistry B* **2017**, *121*, 17, 4319-4332.
6. Gross, Adam S., Alexis T. Bell, and Jih-Wei Chu. Thermodynamics of cellulose solvation in water and the ionic liquid 1-butyl-3-methylimidazolium chloride. *The Journal of Physical Chemistry B* **2011**, *115*, 46, 13433-13440.
7. Zhao, Yuling, et al. Effects of cationic structure on cellulose dissolution in ionic liquids: a molecular dynamics study. *ChemPhysChem* **2012**, *13*, 13, 3126-3133.