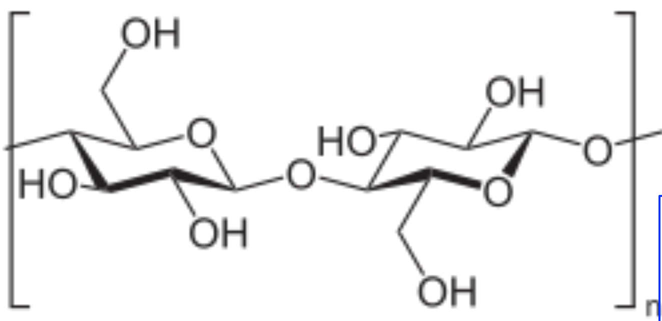
Optimizing the Use of Plant Cellulose as a Liquid Transportation Biofuels Precursor

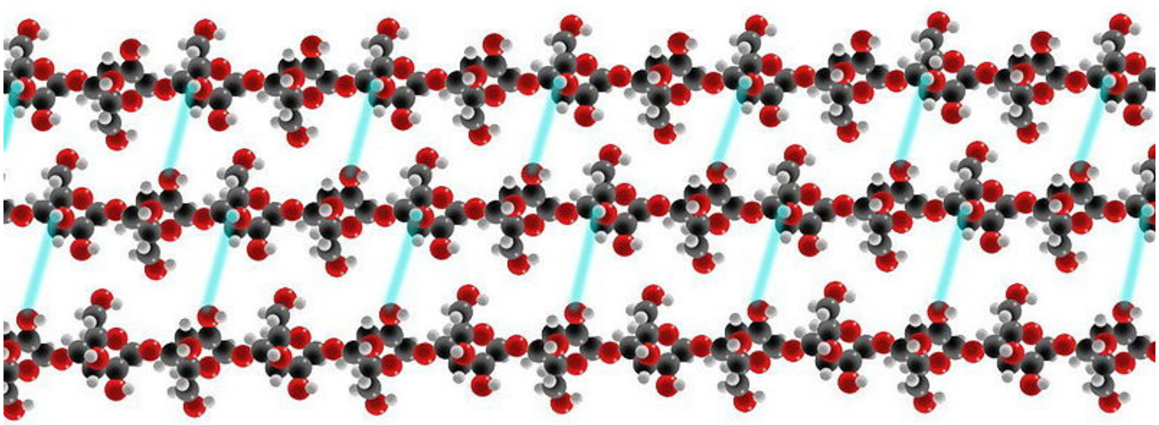
Sandia research paper captures large readership

Background

Cellulose—celery: the relationship is useful to imagine some of the problems in the biofuels industry. Cellulose is abundant in celery, and it's obviously not very soluble in water—and not very digestible by human digestive enzymes and processes (high fiber, low calories). But to use cellulose for biofuels, it must both be solubilized (dissolved) and then efficiently broken down to the individual units—the hundreds of molecules of the sugar glucose—that comprise it. For cellulose is essentially a polymer of glucose, a 6-carbon sugar that many microorganisms readily ferment to ethanol, a liquid transportation biofuel. Plant cell walls are mostly cellulose, but plants also contain lignin and hemicellulose in amounts that tend to depend on their "woodiness." The separation of these components is part of what is considered *pretreatment* of plant biomass prior to use of the component sugars for ethanol fermentation.



Two glucose molecules covalently linked (left). A single chain of cellulose is composed of hundreds of such glucose linkages, and individual extended cellulose molecules are hydrogen bonded (blue lines) together in plant cell walls (below).



Challenge

A recent research paper published by Sandia researchers studied—through molecular dynamics simulations—the dissolution (dissolving) of cellulose in ionic liquids. Ionic liquids are salts in liquid form and have the ability to form stronger bonds with individual cellulose molecules than the weaker hydrogen bonds that normally hold individual

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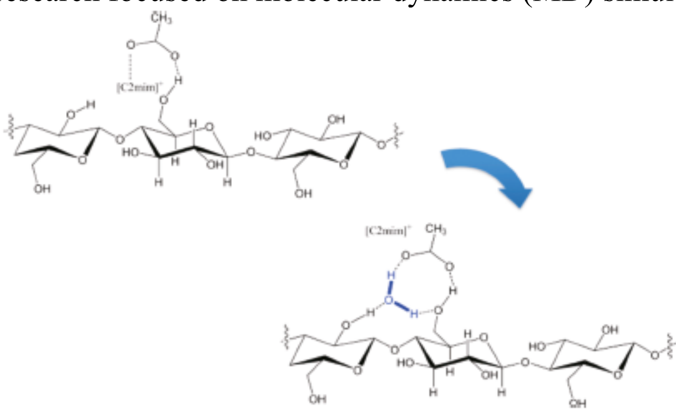
cellulose molecules together. Chemists have known for some time that ionic liquids effectively dissolve cellulose, and that adding water or some other antisolvent (a liquid in which the cellulose is not soluble) will then precipitate the cellulose molecules into a form that is far more amenable to digestion into its component glucose units. In turn, the glucose is then chemically available for fermentation to ethanol. What has remained in doubt is a detailed understanding of the types of intermolecular chemical bonds that are formed between ionic liquids and cellulose, and then the bonding details that ensue when water or another antisolvent is added to the chemical system.

Research

This research focused on molecular dynamics (MD) simulations to study mixtures of the



Proposed key intermediate structure suggested by the simulations of cellulose precipitation from ionic liquids in the presence of an antisolvent such as water.

ionic liquid 1-ethyl-3-methylimidazoliumacetate ([C2mim] [OAc])with water and cellulose. MD simulation provided a detailed analysis of interactions among individual atoms in these systems and how these interactions are altered by changes in the concentrations of the three components (cellulose, ionic liquid solvent, and water antisolvent). Ultimately, the research answered two key questions: identifying the key intermolecular bonding interactions between the ionic liquid and cellulose that promote the dissolving of cellulose and elucidating how water acts as an antisolvent to disrupt those bonding interactions between the ionic liquid and cellulose. The work provides fundamental insights into the molecular-level behavior of this particular ionic liquid ([C2mim][OAc]) in aqueous solutions at various concentrations.

Impact

The insights gained from molecular dynamics simulations in this project were published in the 2011 *Journal of Physical Chemistry B*, and this paper has the distinction of being the most read article in that journal for 2011(J. Phys. Chem. B 2011,*115*,10251–10258). This is indicative of how critical this knowledge about pretreatment is to the biofuels community. Although the researchers studied only one ionic liquid, the knowledge gained about bonding can potentially be extended to other ionic liquids and cellulose. Such detailed knowledge of this chemistry will have a significant impact on the optimization of plant biomass pretreatment, and hence the upfront costs of such pretreatment by comparison to the output of ethanol production, which define both the process' efficiency and its profitability. Because of our ongoing dependence on foreign oil, the production of biofuels that can recycle carbon dioxide and be essentially carbon neutral with respect to the effect of carbon dioxide as a greenhouse gas is a key national security objective. This study is fundamental to optimizing biofuels production from plant biomass, and its widespread readership is evidence of a recognition by the biofuels community of its importance to understanding the detailed chemistry underlying the critical intermolecular interactions.

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