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Supporting Information

Solvent Influence on Cellulose 1,4-β-Glycosidic Bond Cleavage: A Molecular Dynamics and Metadynamics Study

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Supporting Information

Rotation ϕ: Intramolecular hydrogen bond O(2)···O(6')

The intramolecular hydrogen bond O(2)···O(6') is of special importance for the first step of the acid hydrolysis mechanism. Since O(6)H is the most basic hydroxyl group, it might hinder protonation of the glycosidic oxygen, which is the energetically most demanding step of the reaction.[1] The calculated distributions of the O(2)···O(6') distances in water and EmimAc for M1 and M2 are depicted in Figure S1. In water the O(2)···O(6') hydrogen bond is present in M1 and M2. Since the O(2)···O(6') hydrogen bond includes the exo-cyclic O(6') group of the reducing ring, it is more flexible with regard to the distance and can thus be maintained in M1 and M2 in contrast to the O(3')···O(5) hydrogen bond. As expected, the number of intramolecular hydrogen bonds is reduced in EmimAc compared to water: for cellobiose from 36% (water) to 5% (EmimAc) for the O(2)···O(6') hydrogen bond in M1. What are the consequences for hydrolysis? The low population of the O(2)···O(6') hydrogen bond should make protonation of O(1) easier in M2. In M1 on the other hand the O(2)···O(6') hydrogen bond is highly populated and protonation of O(1) is less likely.

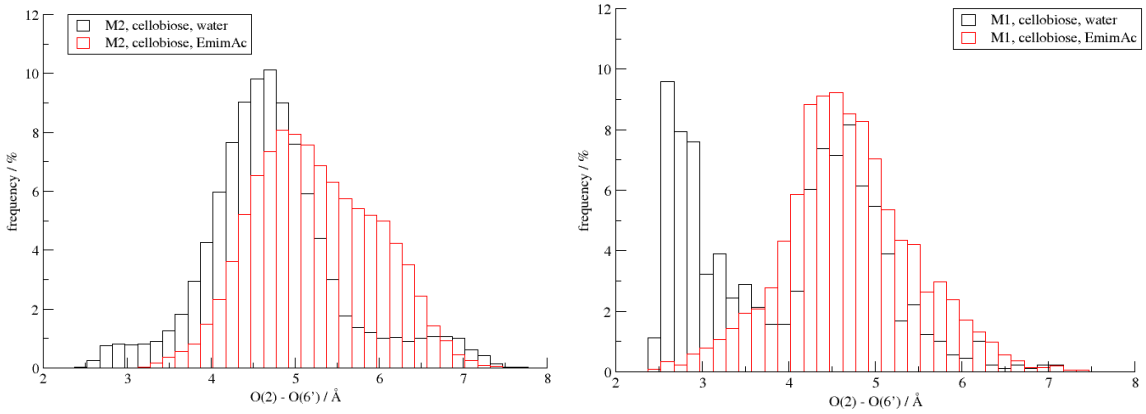

Figure S1: Correlation of the hydrogen bond distance O(2)···O(6') and the dihedral angle ϕ taken from 100 ns molecular dynamics simulations of cellobiose at 420 K in water and EmimAc.

Ring flip α_1 and β_1: Correlation of α_1 and β_1

As the glycosidic linkage is only perfectly axial if both dihedrals β_1 (C(5)-O(5)-C(1)-O(1)) and β_2 (C(3)-C(2)-C(1)-O(1)) are at 90° or 270°, respectively, we correlate them in Figure S2. If β_1 is axial, β_2 is also axial, but this is not true vice versa. Therefore the analysis in the main paper focuses on the more relevant β_1 dihedral.

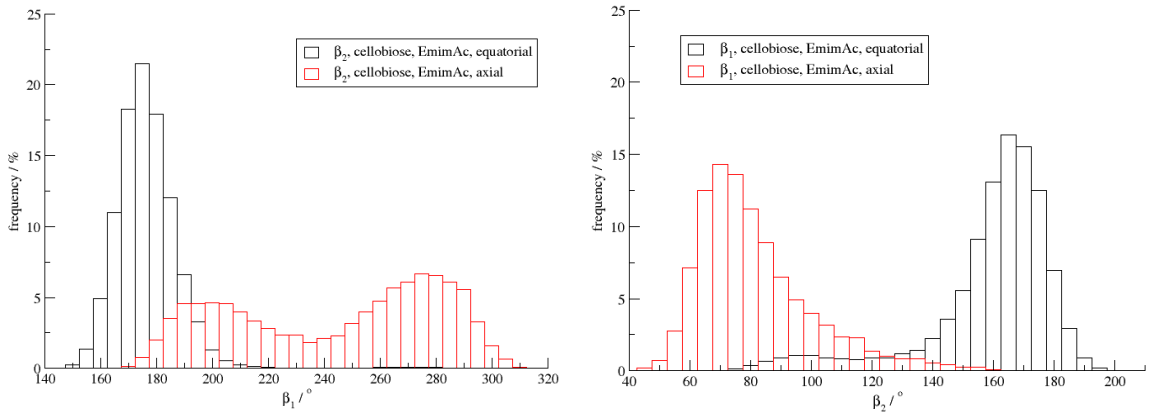

Figure S2: Correlation of β_1 and β_2 taken from a 100 ns molecular dynamics simulation of cellobiose at 420 K in EmimAc.

[1] C. Loerbroks, R. Rinaldi, W. Thiel, *Chem.-Eur. J.* **2013**, *19*, 16282-16294.