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A Computational Study of Cellobiose Hydrolysis in Ionic Liquids

The current environmental situation, with respect to global warming and the ever–approaching depletion of fossil fuel sources, places significance on the development of green fuel and platform chemical production methods. In this context, processes that utilise biomass sources as feedstock, are of great interest. Starchy biomass is an efficient and cost-effective source of glucose and a versatile platform chemical base or biofuel source. However, its use infringes on agricultural production and land usage. Alternatively, cellulose, which is the most abundant biopolymer in nature, is a renewable low–cost carbon resource derived from harvest residues and sources like wood and straw. Thus, it does not directly compete with food production.1 Glucose generation from cellulose requires a saccharide conversion, whereby the β–(1,4) glycosidic bond linkages in the cellobiose polymer repeating units are cleaved. This can be achieved through pyrolysis, enzymatic as well as acidic hydrolysis. The enzymatic route is the most efficient but limited in extent due to cost and the narrow range of solvents and reaction conditions needed. On the other hand, problems arise in the hydrolysis of cellulose where firstly, experimental and theoretical studies have shown cellulose to have very low solubility in water and most other general molecular solvents.1 This results in the use of harsh pre-treatments at high temperatures and pressures to extract cellulose from lignocellulosic material. Secondly, a substantial energy barrier is observed for the reaction under aqueous conditions necessitating the use of strong acids (pKa < −3.2).2 Overall, this renders the process costly, inefficient and counterintuitive to its overall environmentally–friendly purpose.

Recently, a favourable medium of cost efficiency and potential environmentally friendliness has been found in the use of ionic liquids (ILs).3 ILs are salts with low melting points that consist of organic cations and inorganic or organic anions and have the potential to be eco–friendly, designer solvents.3 It has been shown that ILs can dissolve cellulose under relatively benign conditions and can possibly be adapted into a one-pot-like process of hydrolysis using acid functionalised ILs.4,5 This study aims to investigate theoretically the effect of an ionic liquid in the mechanism and thermodynamics of the acid hydrolysis of cellobiose, both as a solvent and as a catalyst. The effect of different Brønsted acid functionalized ionic liquid cations on free energy of protonation, and a comparable measure of acidity for these acidic ILs, are presented. DFT computations using implicit models, such as the generic and partially generic solvation model based on density, SMD-GIL and SMD-PGP,6 were extended to hybrid implicit-explicit techniques, using approaches such as a cluster-continuum method,7 allowing for an assessment of the accuracy of implicit representation of ionic liquid solvation.

The proprietary Gaussian09 and free ORCA 4.0.1 software packages were used, the former using TCP LINDA and the latter with a parallel implementation based on OpenMPI. Calculations used at most 24 cores on a single node, in line with the scaling behavior of typical molecular QM codes.

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Presenter Biography

Primary authors: Ms NEL, Jessica (University of Cape Town); Dr VENTER, Gerhard (University of Cape Town)

Presenter: Ms NEL, Jessica (University of Cape Town)

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