

A Combined Computational And Experimental Investigation of the Dissolution of Chitin in Organic Electrolyte Solutions

Abstract:

While fossil fuels are the primary source of energy used to power homes, business, cars, etc., its resources are rapidly decreasing as a result of broad and extensive use.¹ Moreover, the burning of fossil fuels results in severe environmental pollution.² For this reason, sustainable and environmentally friendly production of biofuels, which can be derived from biomass such as cellulose, chitin and chitosan, have attracted great interest in the past decade.³

Chitin can be isolated from the cell walls of fungi, the exoskeletons of some insects as well as certain crustaceans which makes it a highly sustainable and virtually inexhaustible source of energy.⁴ Unfortunately, dissolving biomass with water or common organic solvents at moderate reaction conditions, is challenging as its intermolecular and intramolecular hydrogen bonding network and interlayer dispersion interaction is too strong to be easily disrupted.⁵ For this reason, specialist solvent systems such as ionic liquids (ILs) have recently been considered for biomass dissolution.

Ionic liquids are molten salts consisting of an organic cation that is poorly coordinated to an inorganic/organic anion and is liquid below 100 degree Celsius.⁶ Very promising results have been shown by using ILs with anions that have strong hydrogen bond accepting ability, such as 1-butyl-3-methylimidazolium acetate, although the cation is known to play an important role and can render the anion ineffective.⁷ In addition, due to the strong electrostatic interaction between the cation and anion, ILs are typically highly viscous, which can impact the effectiveness of dissolution. Adding an additional molecular solvent (a co-solvent) to the ionic liquid and therefore creating an organic electrolyte solution, has been an effective measure to decrease the electrostatic interaction between the cation and anion, which then often leads to better dissolution properties.⁸ However, there is no routine theoretical procedure that can accurately predict which co-solvent/IL combination will work best, aside from costly experimental verification.

In this work, we present potential of mean force (PMF) calculations for separating two methyl-N,N'-diacetylchitobiose molecules in various organic electrolyte solutions as a model to represent the dissolution of chitin, rather than a larger microcrystal, as this would be computationally too demanding. The solvent systems chosen were pure 1-butyl-3-methylimidazolium acetate, propylene carbonate, dimethyl carbonate and γ -valerolactone, as well as 2:8 and 8:2 mixtures of these co-solvents with the ionic liquid. The co-solvents were chosen as they are considered to be "green" and environmentally friendly alternatives to harsh organic solvents. Results will be discussed and compared to experimental results.

References

1. Höök, M.; Tang, X. *Energy Policy* **2013**, 52, 797-809.
2. Pollution Caused by Fossil Fuels <https://education.seattlepi.com/pollution-caused-fossil-fuels-4776.html> (accessed Aug 30, 2018).
3. Japanese team cracks into biofuel with crab shells <https://asia.nikkei.com/Tech-Science/Science/Japanese-team-cracks-into-biofuel-with-crab-shells> (accessed Aug 30., 2018).
4. Alonso, D.; Wettstein, S.; Bond, J.; Root, T.; Dumesic, J. *ChemSusChem* **2011**, 4, 1078-1081.
5. Klemm D.; Heublein, B.; Fink, H.; Bohn, A. *J. ChemInform.* **2005**, 44, 3358-3393.
6. Seddon, K.; Rogers, R. *Science* **2003**, 302, 792-793.
7. Mohd, N.; Draman, S.; Salleh, M.; Yusof, N. *AIP Conf. Proc* **2017**, **1809**, 020035.
8. Rinaldi, R. *Chem. Commun.* **2011**, 47, 511-513.

HPC Content

Potential of mean force calculations were performed with the AMBER PMEMD CPU code at the CHPC. This is one of the fastest MD codes available with a highly efficient MPI implementation and the option of an even more efficient GPU implementation. Simulations were limited to 64 processors across four nodes without

high memory requirements. Array jobs, consisting of 13 independent windows of 50 ns, were used for each simulation. More than 10 array jobs were used in order to model all solvents systems, which equates to more than 130 batched jobs and 6.5 μ s of simulation.

Presenter Biography

Primary author: Mr CARROLL, Lenard (University of Cape Town)

Co-authors: Dr JARDINE, Anwar (Department of Chemistry, University of Cape Town); Dr VENTER, Gerhard (Scientific Computing Research Unit and Department of Chemistry, University of Cape Tow)

Presenter: Mr CARROLL, Lenard (University of Cape Town)

Session Classification: Poster session

Track Classification: Computational Chemistry