Thermodynamics of the interaction of monosaccharides and halloysites

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Abstract

Halloysites are often integrated within polysaccharide films as drug carriers and to tune their mechanical properties. One of the most important aspects of these composites is the mineral-organic interface, which will have an important impact on the material properties. Here we investigate the thermodynamics of binding of multiple saccharides onto halloysites using molecular dynamics simulations.

Objectives

- Analysis of monosaccharides binding onto halloysite silicate surface:
  - Acetylglucosamine – neutral.
  - Glucosamine – neutral.
  - Protonated glucosamine –positively charged.
  - Mannuronate– negatively charged.
- Investigation of the thermodynamics of the process.

Conclusions

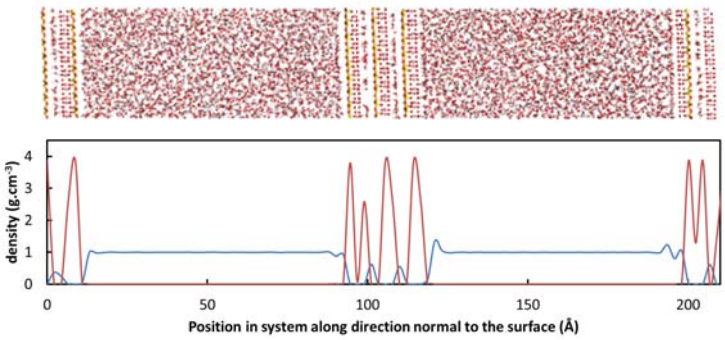
- All saccharides show a favourable binding energy to the halloysite surface.
- The main driving force is enthalpic.
- For protonated glucosamine, the positively charge amine group does not interact with the surface.
- Future work will look into the free energy of attachment of water molecules and the change of modes of the saccharides to understand which of the two is the biggest factor in the unfavourable entropic change.

Methods

- Molecular Dynamics simulations.
- Force fields:
  - Halloysite – CLAYFF[1].
  - Water – SPC/F[2].
  - Saccharides – AMBER GLYCAM[3].
- Umbrella Sampling at different temperatures to obtain enthalpic and entropic change.

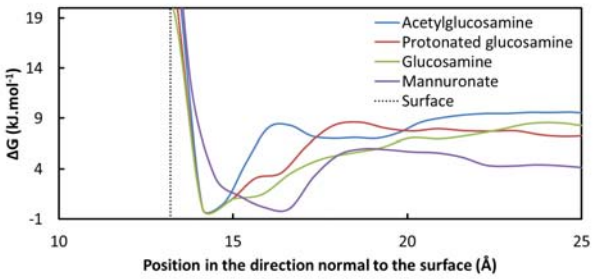
Equilibrated system and water density in the system

- To remove the dipole arising from the halloysite surface, the system is increased in size and an additional surface in the opposite direction is inserted.
- The water shows some structuring at the hydroxyl side, but only a slight inflection at the silicate surface. This is the external surface of the halloysite where saccharides will bind.

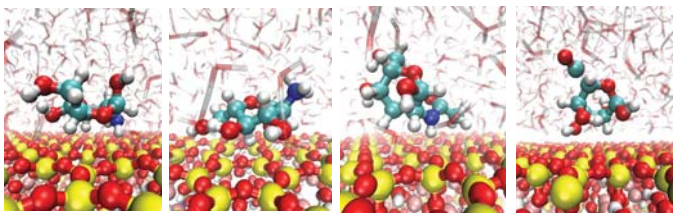


Free energy of binding and stable configuration on halloysite surface

- All saccharides show a favourable free energy of binding. No transition barrier is observed, probably due to the weak interaction of the water at this surface. The strongest binding is observed for acetylglucosamine while the weakest was obtained for mannuronate.
- Simulations at different temperatures showed that the binding is driven by the change in enthalpy. For instance , for chitin ΔH is exothermic with a value of -61.7 kJ.mol^{-1} while ΔS decreases of -0.174 kJ.mol^{-1}.K^{-1}.



- Saccharides interact mainly via neutral groups with the surface, while the polar groups remain in solution. The latter, probably, have a stronger interaction with the water molecules.



Glucosamine | Protonated Glucosamine | Acetylglucosamine | Mannuronate

References

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