# Understanding the Thermodiffusion Properties of Ionic Solutions in the Presence of Cellulose Fibers

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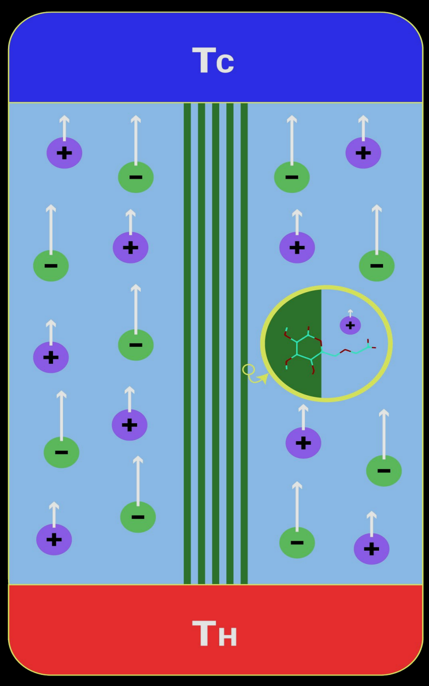
## Introduction:

The search for green energetic devices grows daily. Cellulose, as the most abundant organic molecule plays an important role in that.
Besides that, ionic solutions are also a great ally for those applications, once that it produces large quantities of free-charge, which can be used for storing and generation of energy.

To analyse the ion-cellulose interaction, all-atom simulations were performed. We based our simulated system on thermionic papers recently synthetized [1]. For that we modified cellulose fibers in many concentrations; carboxymethyl groups were added and their interactions with ions was analysed.




The role of polymers in thermophiles is to increase their efficiency, interacting with ions, and enriching the solution Seebeck effect.[2]

## Methodology:

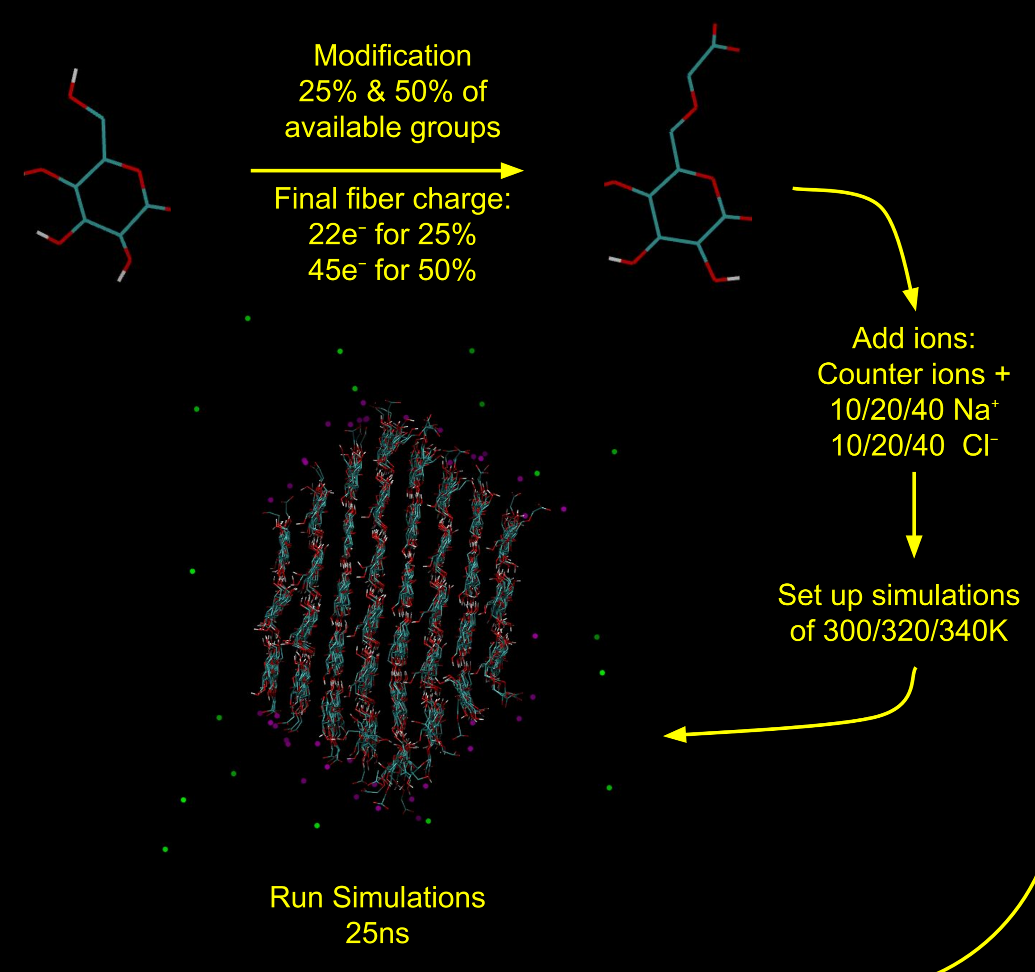
Computational Details:

Simulation Software:
- GROMACS [3]

Force Field used:
- GROMOS 53a6glyc [4]

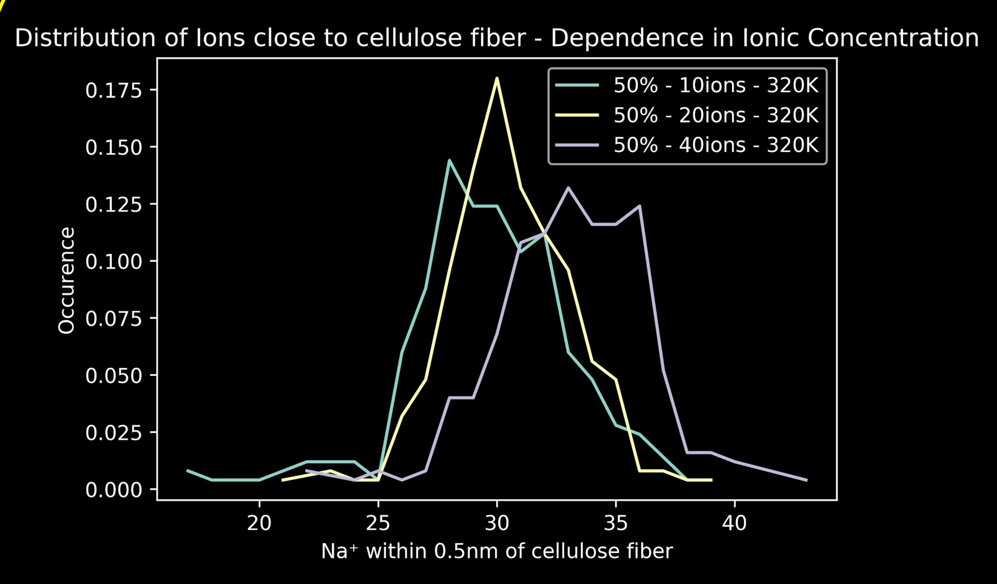
Parameters of Interest [5]:
- Solvation Energy
- Soret Coefficients for an ion and salt
- Seebeck Coefficient
- Their dependence on fiber modification percentage and ion disponibility.

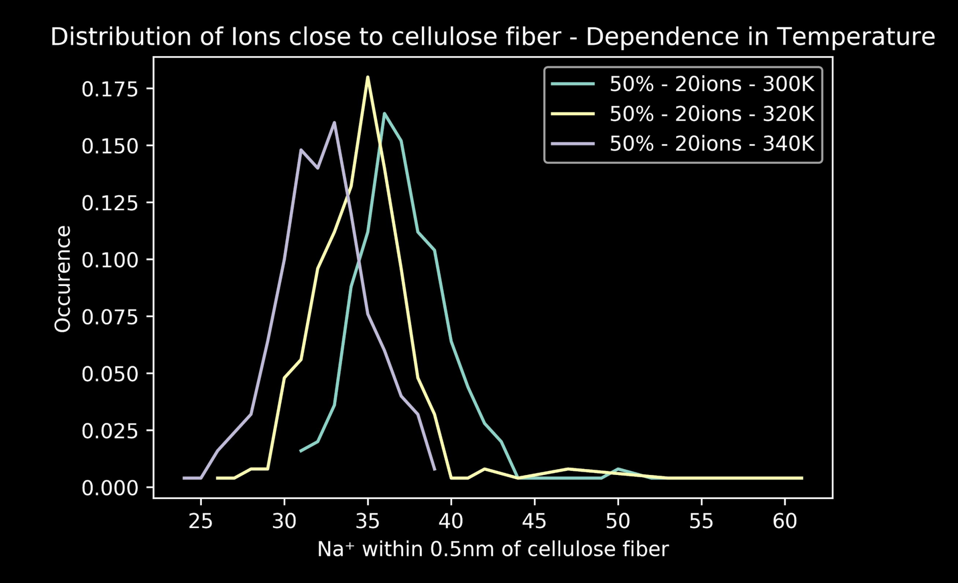
Simulation Protocol:



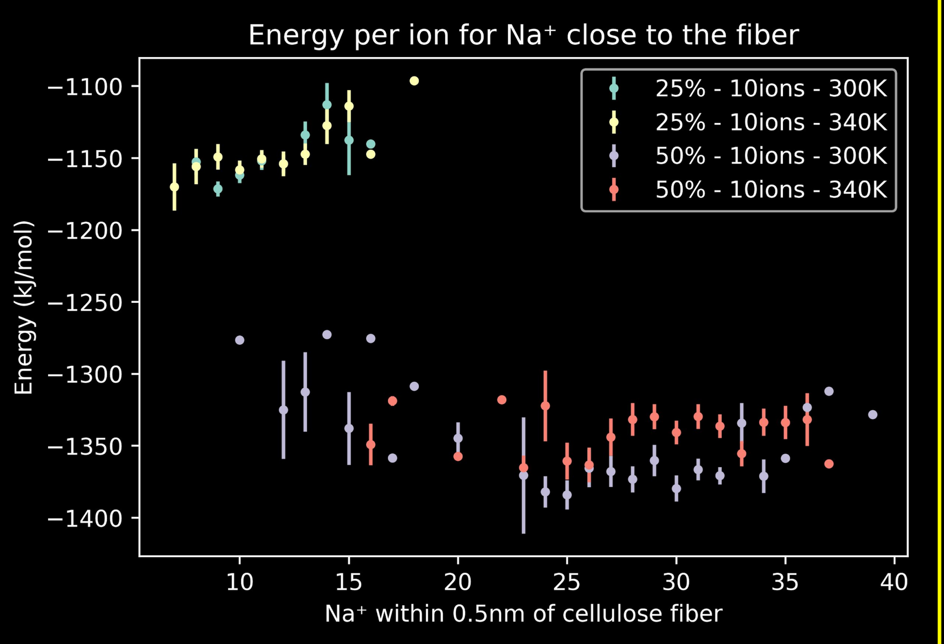

## Results

### Cellulose - Ion Interaction

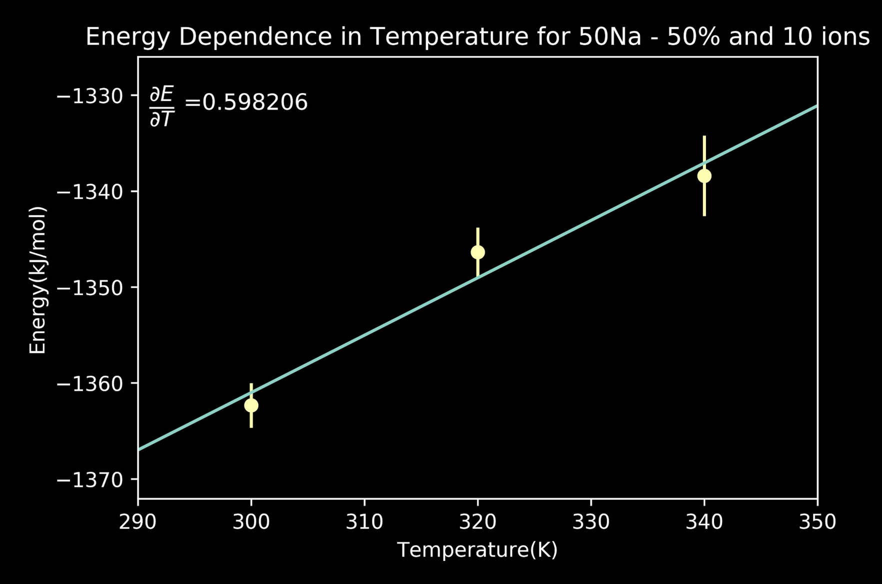



It is possible to see that the expected value of ions close to the fiber has a small variance in different temperatures and ionic concentration. The highest temperature, less ions interacting with the fiber, the highest ionic concentration, more ions interacting.



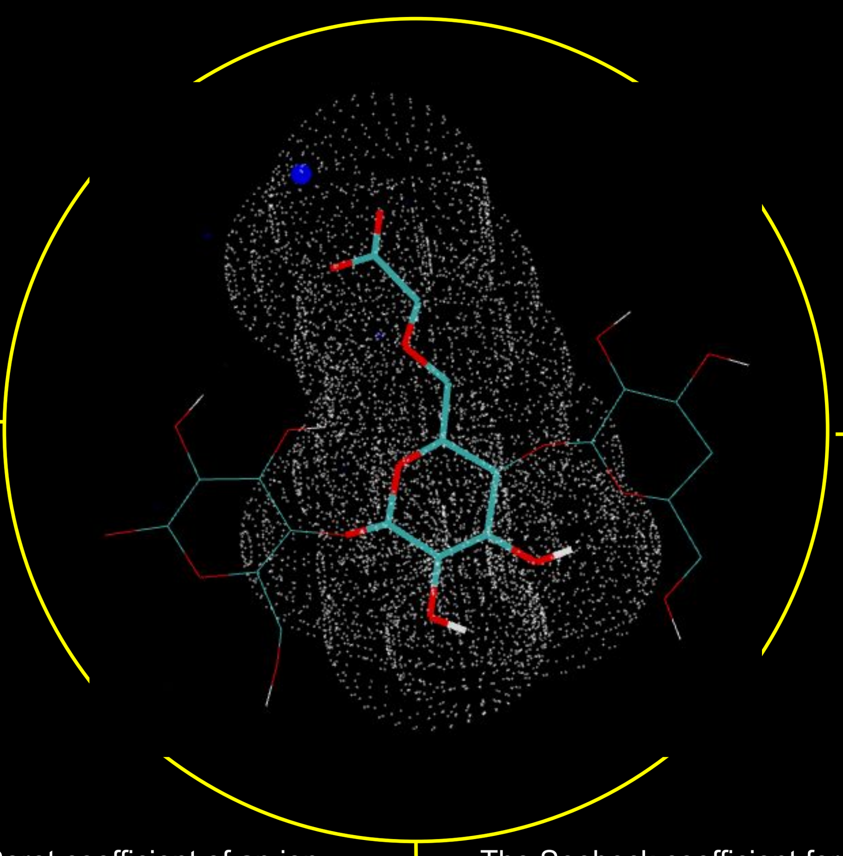

Analysing the ionic energy variation in relation to the quantity of ions next to the fiber, we can see that although we expect different quantity of ions close to the fiber depending on temperature and ion availability, their average energy is constant in some intervals. As a result of that the mean value of energy was computed using frames of [10-14] ions for 25% modified fibers and [29-33] for 50%.




Different values for the angular coefficient were obtained depending on the system properties. For Cl⁻ their energy variations close to the fiber were not computed because just few configurations had Cl⁻ within this distance from the fiber A table is shown with all linear coefficients of the fitted lines:

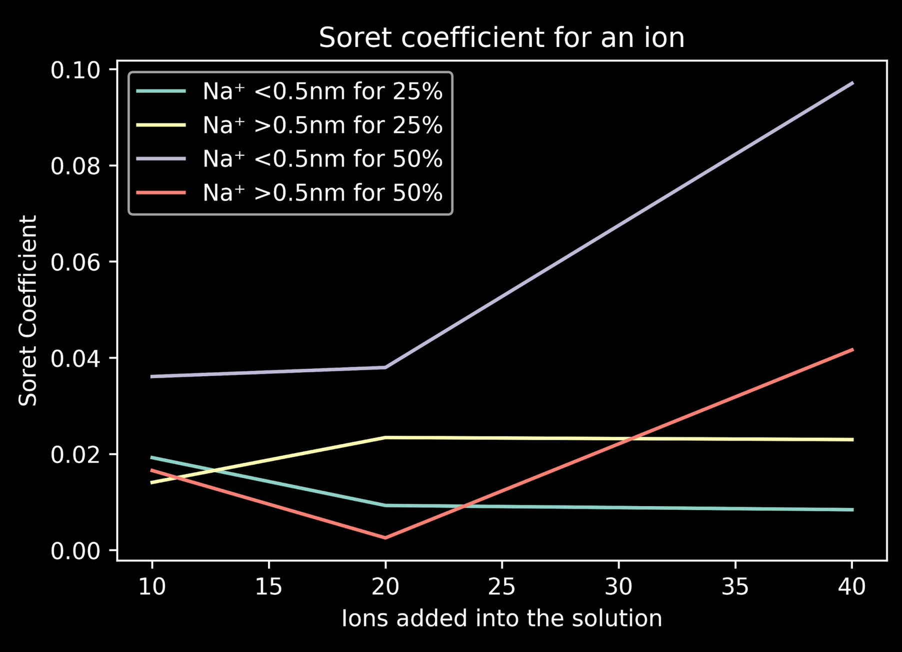
| | $Na^+$ <0.5nm (kJ/mol) | $Na^+$ >0.5nm (kJ/mol) | $Cl^-$ >0.5nm (kJ/mol) |
|---|---|---|---|
| 25% - 10 ions | 0.31 | 0.23 | -0.03 |
| 25% - 20 ions | 0.15 | 0.39 | 0.13 |
| 25% - 40 ions | 0.14 | 0.38 | 0.12 |
| 50% - 10 ions | 0.60 | 0.27 | 0.17 |
| 50% - 20 ions | 0.63 | 0.04 | 0.40 |
| 50% - 40 ions | 1.61 | 0.69 | 0.24 |

Those values were used as an approximation for the free energy variance no our system, used thus to compute the Soret coefficients.



### Soret Coefficients

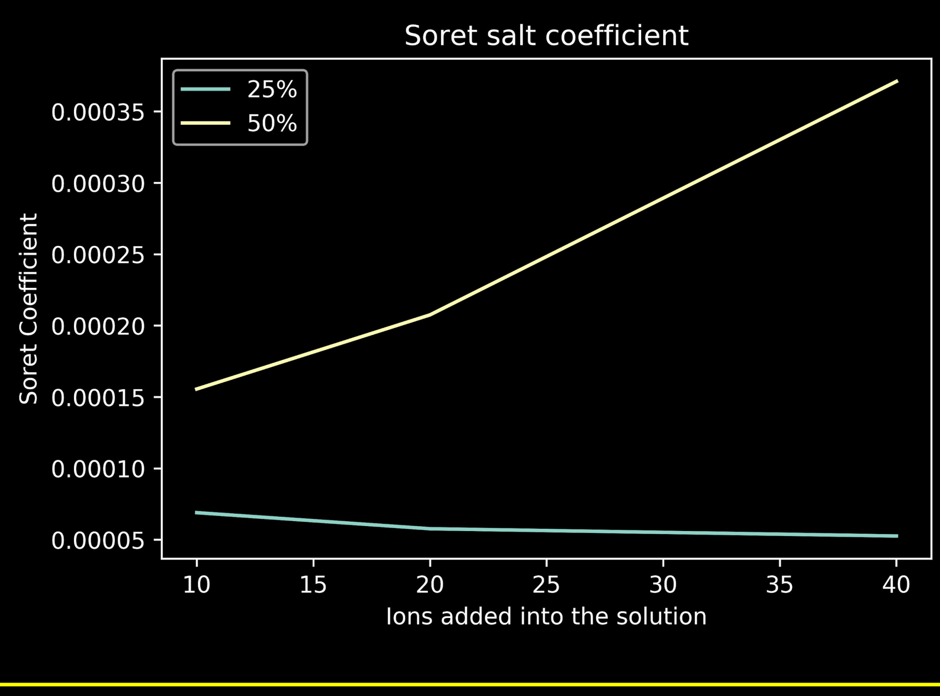
$$\alpha_{\pm} \approx \frac{1}{2k_B}\frac{\Delta E}{\Delta T}$$




For the Soret coefficient of an ion it is possible to see that the energy variances for 50% fibers is much higher than for 25%. This shows us that the less modified fiber doesn't have main changes on its interaction with ions due to an increase of ion availability.

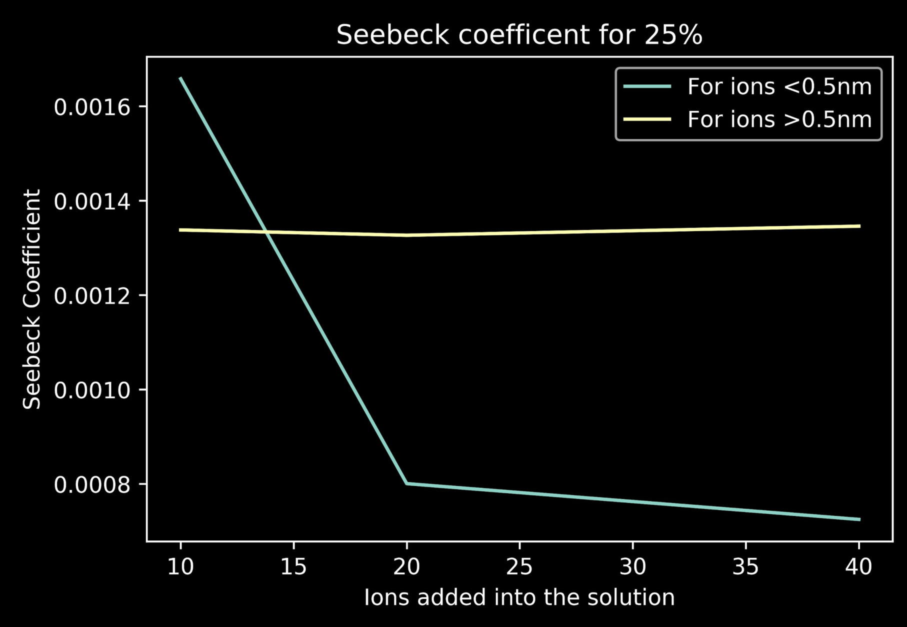
$$\alpha = \frac{1}{T}(\alpha_+ + \alpha_-)$$

The salt Soret coefficient represents the first relation made between positive and negative ionic energies. It shows that the 50% modified fiber increases its Soret coefficient when we increase the ionic availability, while the 25% fiber had decreased smoothly.

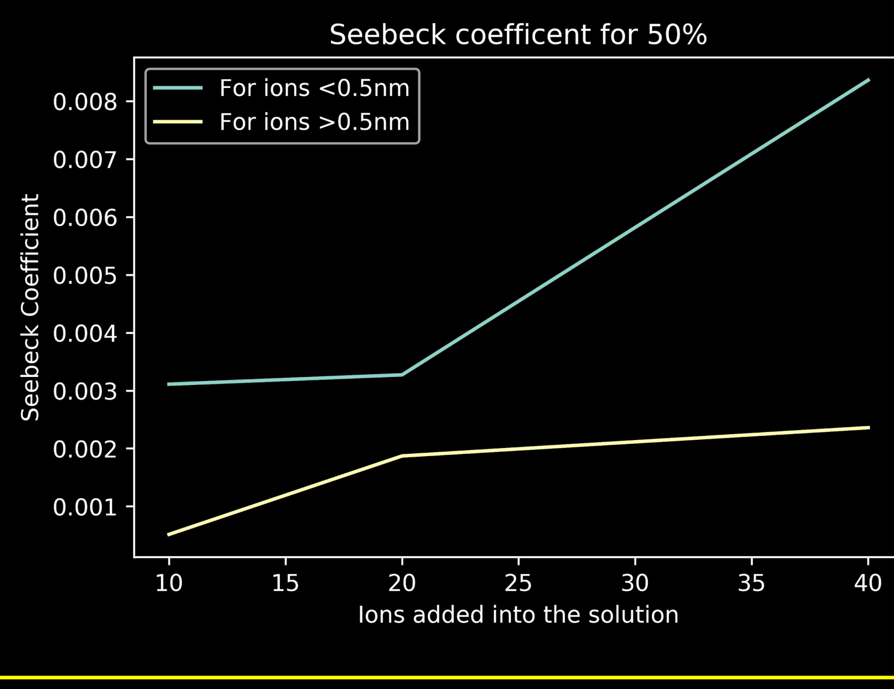



### Seebeck Coefficient

$$S = \frac{k_B}{e}(\alpha_+ - \alpha_-)$$




The Seebeck coefficient for 25% was computed and a decreasing behavior was noted. It is interesting to note that for distant ions the increase of concentration has almost no effect on its Seebeck values, showing that the ions in solution barely feel the fiber electric potential.




For the 50% modified fiber the behavior was the opposite, the Seebeck coefficient had an increase for higher ionic concentration. Besides that the Seebeck for $Na^+$ in solution had an initial growth on its value, showing that for small concentrations of ions in the solution, the electrical charges of fibers still affects its environment.

## Conclusions:

- The interaction between cellulose and ions on an aqueous medium was successfully analysed, the main results are related to whether and how the energy changes depending on ionic concentration, temperature and modification level of cellulose fibers.
- The increase of Seebeck coefficient in ions next to the fiber, desired to the advance of green energetic devices, was just observed on the fiber modified by 50% and the difference was greater in higher ionic concentrations.
- For the 25% modified cellulose the observed was the opposite, the Seebeck coefficient decreased with the increase of ionic concentrations, and was just higher than the ions in solution for the lowest concentration.
- More investigation is still necessary to better understand how this change in the behavior occur and what affects it. As a next step, we intend to apply the same methodology to intermediary levels of modifications and also for a broader range of ionic concentration.

## Acknoledgements:

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## References:

[1] Fei Jiao, et. al. (2017) Journal of Materials Chemistry. 5, 16883-16888.
[2] Dan Zhao, et. al. (2019) Nature Communications. 10, 1093-.
[3] Berendsen, et al. (1995) Comp. Phys. Comm. 91, 43-56.
[4] Laercio Pol-Fachin, et al. (2012) J. Chem. Theory Comp. 8, 11, 4681-4690.
[5] Sehnem, et. al. (2018) J. Phys. Chem. B. 122, 4093-4100.