Unveiling the role of solvent in gelation via a novel solution state NMR protocol

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BACKGROUND

STD NMR is a well-established methodology for the study of protein-ligand interactions in biological systems.[1] Nonetheless, the application of STD NMR in Material Science is not yet well explored. In this regard, the accurate STD NMR characterisation of solvent-particle interactions and their role on gelation is limited by the strong dependence of the STD intensities on solvent and gelator concentrations.

This precludes the correct determination of the degree of solvent structuration within gel networks. In hydrogels, water constitutes between 90-99% of the system and play an important role in gelation

The SDTD (Spin Diffusion Transfer Difference) protocol is a robust and easy-to-implement NMR method to characterise the degree of solvent structuration in gels.

OUR PROTOCOL
1) STD normalisation
2) Fit to 1D diffusion model

ABSOLUTE STD   VS   NORMALISED STD

EXPERIMENTAL SESSION

Analysis carried out in NMR usually require the employment of deuterated solvent, such as D_2O.

When comparing between different samples, three main factors must be taken into consideration, which affect the amount of protonated solvent (ligands).

1. **Purity** of the **used chemicals**;
2. The **amount of exchangeable protons** in the polymers;
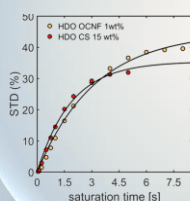3. **Humidity** and exposition to open air

H$_2$O titration experiments

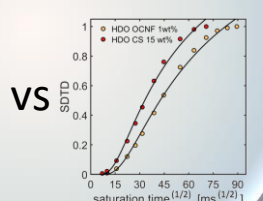STD factors decrease with increase of HDO concentration
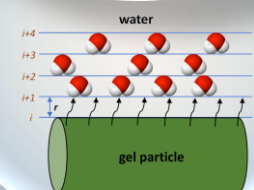
SDTD signal is **not** affected by the HDO concentration
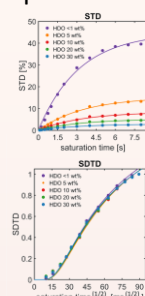
The build-up curve is simulated by mathematical fit

While changes in the STD absolute value upon increment of **gelator concentration** correlate to an increase of the solvent **fraction of bound**[2], the **SDTD factor** is **independent** from gelator concentration.

Comparison of non-charged enzymatically produced cellulose (EpC, 1) and charged oxidisedcellulose nanofibrils (OCNF, 2) reveals the ability of SDTD protocol to **report** about **changes** in the **solvent structuration** around the polymeric network.

(1)

(2)

In OCNF, HDO possibly **structures** around the negative charges to **shield** the electric repulsion, allowing network entanglement.[3]

## CONCLUSIONS

We extended the applicability of STD NMR to characterise solvent interactions to large particles. We demonstrated that the SDTD build-up curves are **(i)** *independent from ligand concentration*, **(ii)** *independent from gelator concentration*, and **(iii)** *report on the degree of solvent structuration*. **SDTD** presents several advantages over other NMR methods to characterise solvation properties. as it can be employed to study diluted dispersions and the simultaneous characterisation of the degree of structuration of various solvents in cosolvent gels. In SDTD the well-resolved solvent peaks are monitored, allowing for the rapid acquisition of the STD build-up curve using routine NMR spectrometers
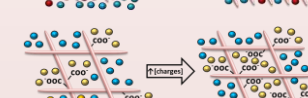
(i)
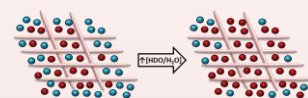
(ii)
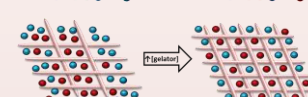
(iii)

[1] Mayer, M., and Meyer, B. (1999) Angew. Chem. Int. Ed., 38, 1784-1788.

[2] V. Calabrese, J. C. Muñoz-García, J. Schmitt, M. A. da Silva, J. L. Scott, J. Angulo, Y. Z. Khimyak and K. J. Edler, *J. Colloid Interface Sci.*, 2019, **535**, 205–213.

[3] J. Schmitt, V. Calabrese, M. A. da Silva, S. Lindhoud, V. Alfredsson, J. L. Scott and K. J. Edler, *Phys. Chem. Chem. Phys.*, 2018, **20**, 16012–16020.

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