NMR study of organic ligands at the AZO nanoparticle surface

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1. Introduction

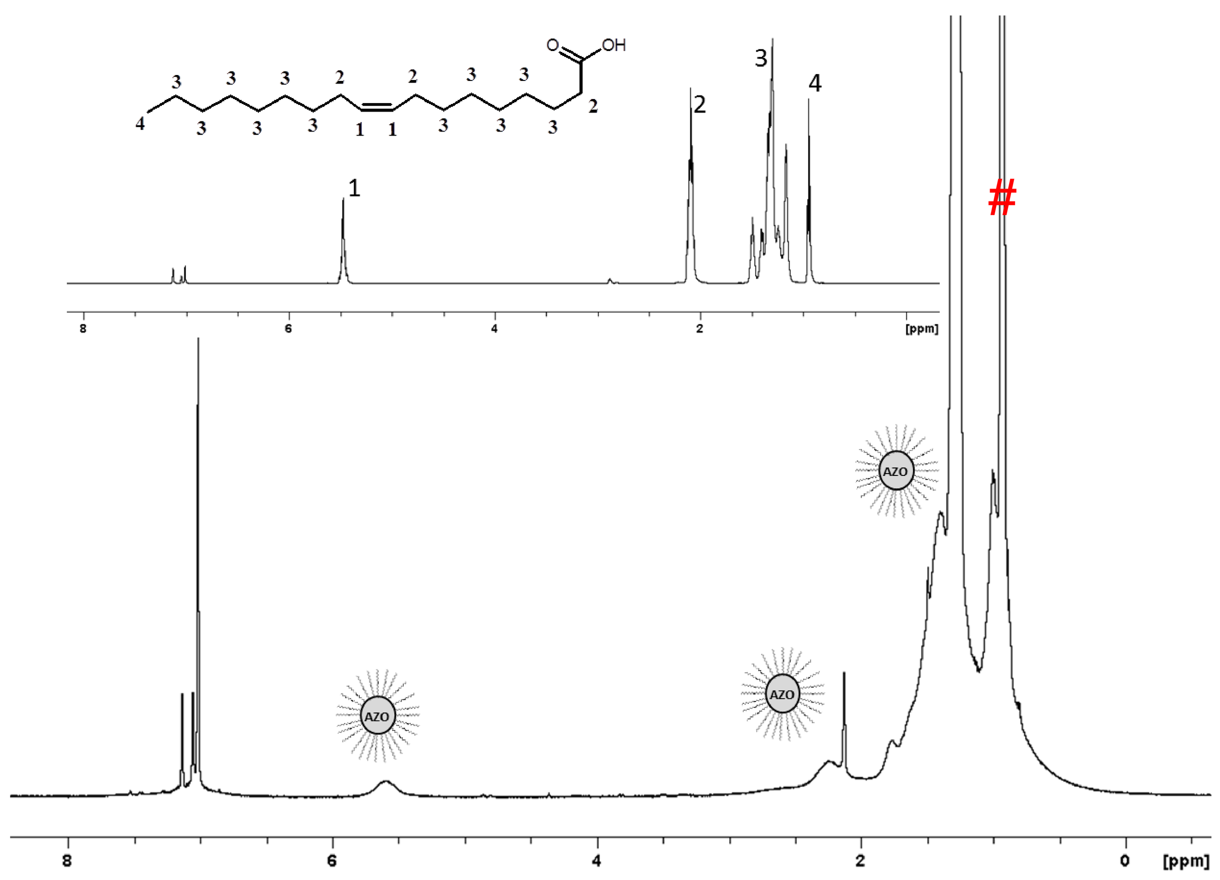
Ligands provide physicochemical functionality to colloidal nanoparticles (NPs). Used during synthesis to control nucleation and growth, they end up as a monolayer covering the NP surface and stabilizing the NP colloidal suspension [1]. After synthesis, they can be exchanged by others to change the properties of the suspension or to improve certain characteristics [2]. In the last few years NMR techniques have been developed that can give a molecular view on the NPs from the ligands' point of view, both in a qualitative and quantitative way. Using this 'NMR toolbox' different NPs and ligands have already been investigated [2-5]. In current research we are focusing on Aluminium-Zinc-Oxide NPs (AZO-NPs) surrounded with oleic acid ligands.

2. Materials and methods

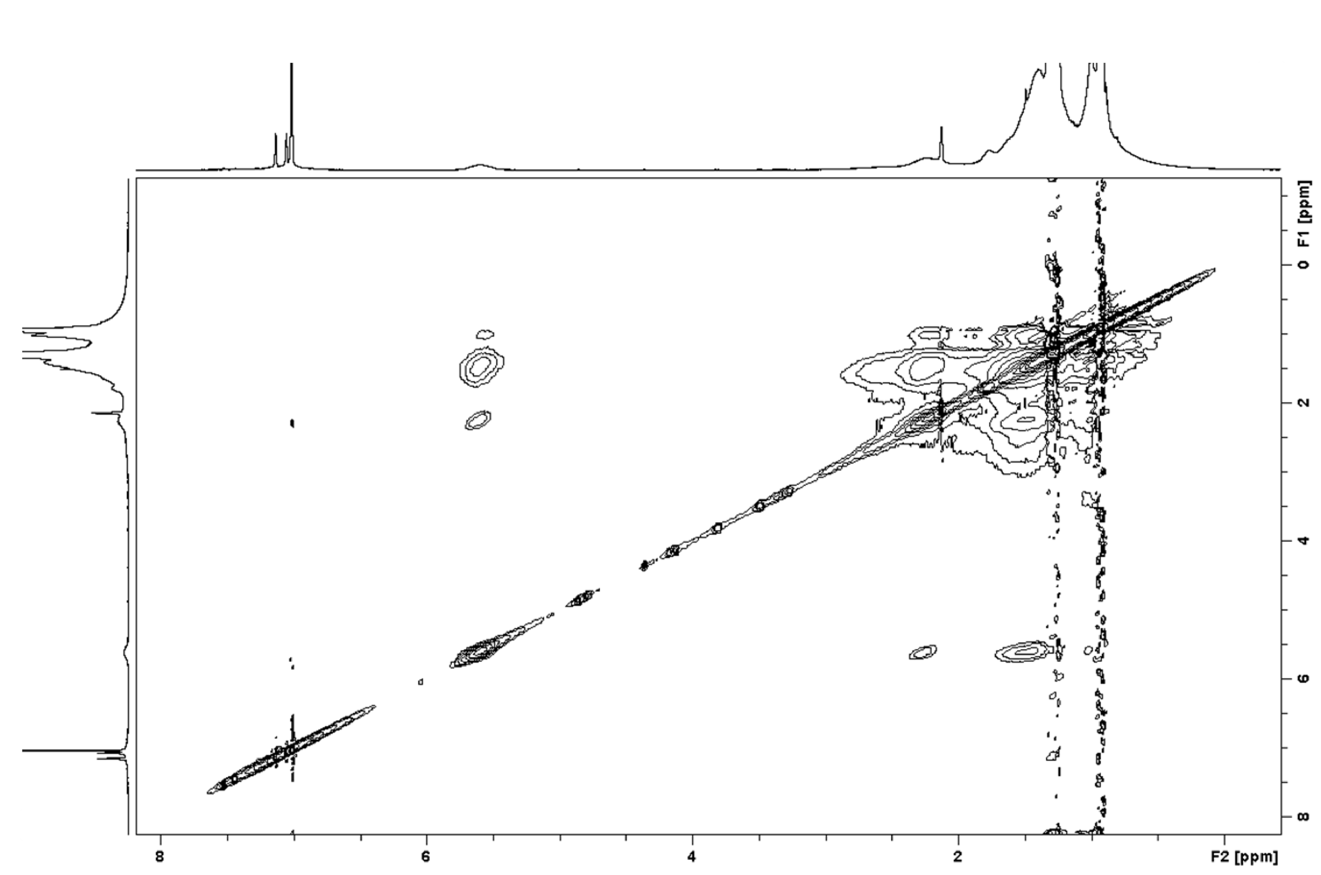
The Aluminium-Zinc-Oxide NPs were synthesized at the university of Hasselt with oleic acid used as a ligand to stabilize the NPs in suspension. The synthesis was performed in toluene which was afterwards evaporated and the NPs were redissolved in toluene-d8 and put in a 5 mm NMR tube.

All the NMR measurements were recorded on a 500 MHz AVANCE spectrometer (Bruker) at ambient temperature. The DOSY and NOESY experiments were set up as previously described in literature [4].

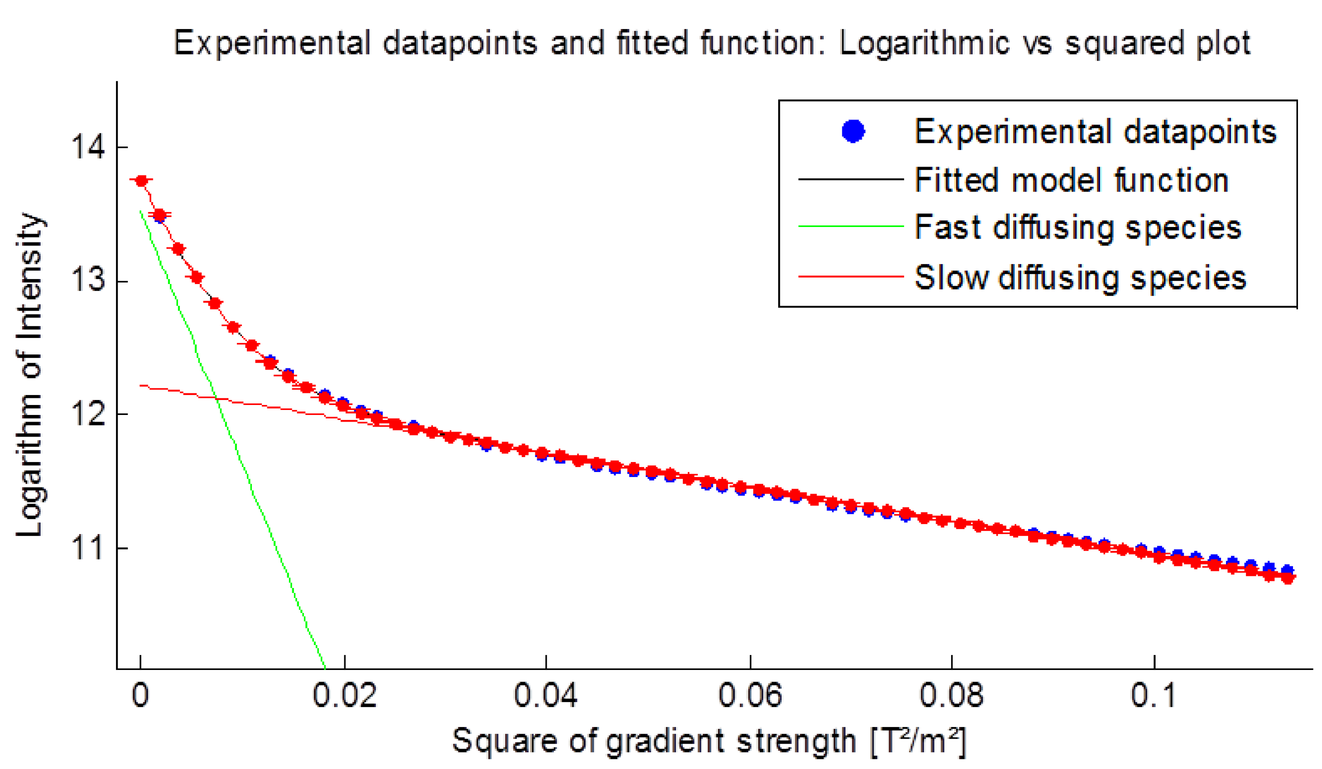
3. 'NMR Toolbox' for investigating NPs



1D ^{1}H: broad resonances and slightly shifted chemical shifts show that the ligand, Oleic Acid (OA), is bound on the AZO NP surface. Extra sharp signals correspond to hexane left-over from the work-up of the sample, or from toluene, used as solvent.



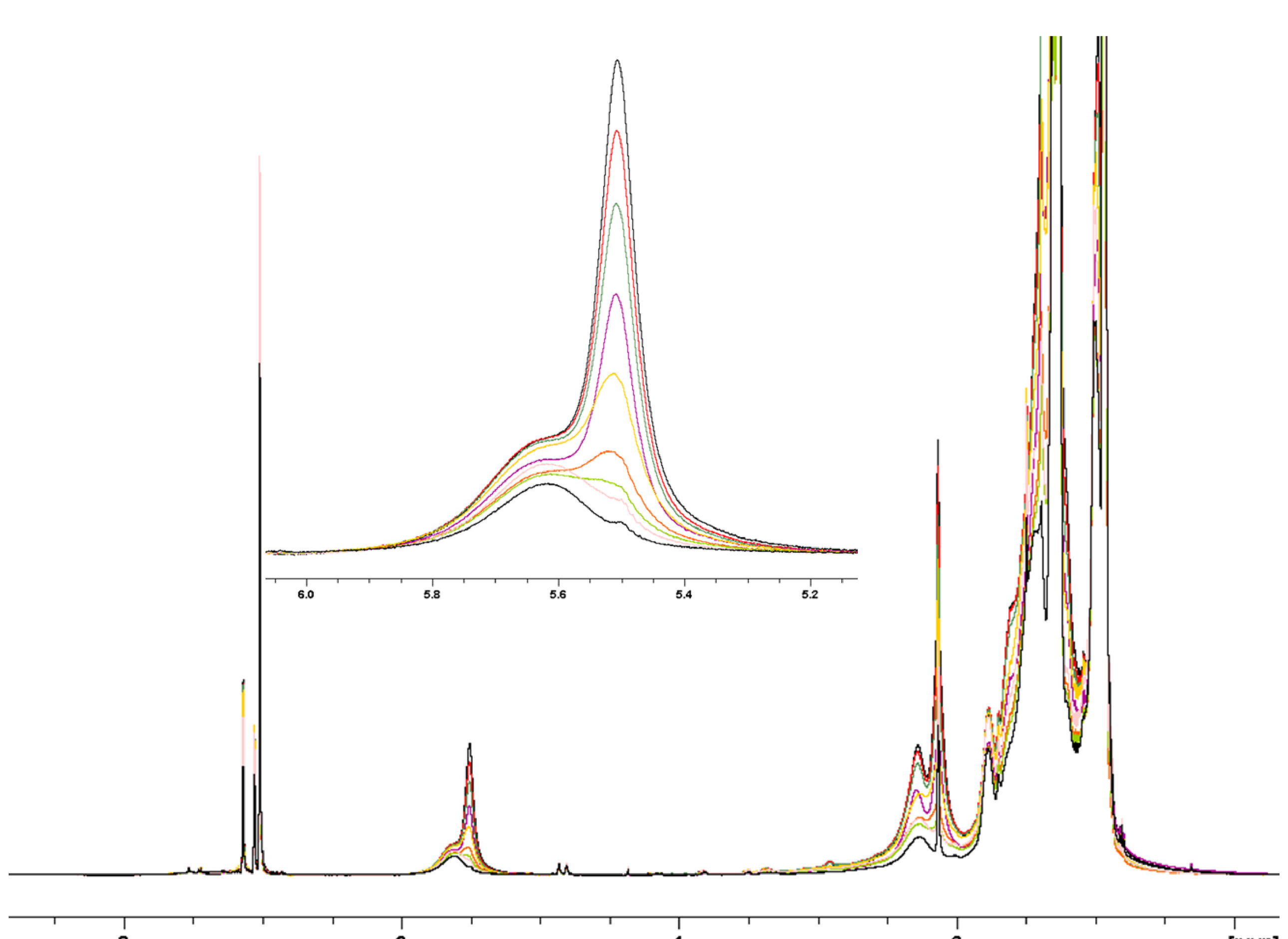
NOESY: strongly negative NOE connecting the different protons of OA show that the OA is tightly bound. These strong negative signals can only build up if the ligand behaves as a large molecule. Note the absence of such NOEs between toluene and hexane resonances.



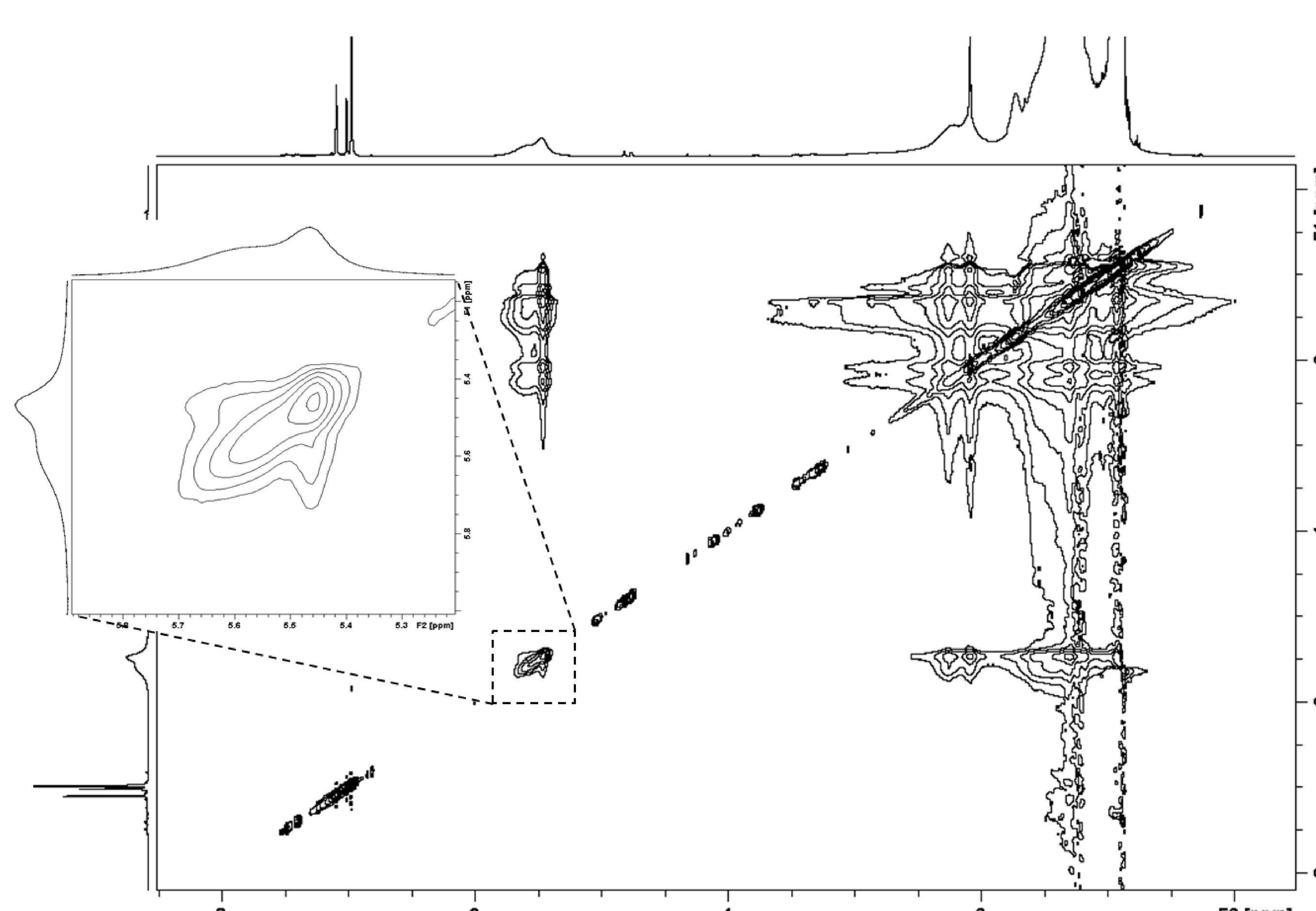
DOSY: At the selected frequency position (see # 1D) the contribution from a rapidly (hexane) and more slowly diffusing species consisting of the OA bound to the AZO-NP, is evidenced. A biexponential function is used to calculate the two different diffusion coefficients.

4. Titration experiment to study the surface chemistry

Free ligand, oleic acid, is added to the AZO-NP suspension.
This in order to see if there is an interaction between bound and free ligand and whether exchange is present.



1D ^{1}H: when adding free ligand to the mixture, we see a "shoulder" arising on top of the broad signal that increases with added OA. This peak does not show a finestructure as expected for free oleic acid, thus it does not behave entirely as a free ligand in solution. Its diffusion coefficient however is almost identical to that of free OA (not shown).



NOESY: Besides the strong NOEs connecting the different protons of the bound ligand, also those of the free ligand are connected, this shows that these also spent time at the surface. The negative cross-peak connecting the bound and new signal of the OA alkene protons is most probably an exchange peak. (to be confirmed by ROESY)

5. Conclusions

The surface chemistry of oleic acid at a AZO-NP is probably more complex than expected. Inconsistent results are obtained when observing the system and adding extra ligand. The diffusion coefficient of the added oleic acid is almost equal to that of free oleic acid in toluene, yet the absence of fine structure in the new oleic acid resonance, the negative NOEs connecting its resonances and a probable exchange peak between the bound and new ligand signals indicates some interaction is going on with the AZO-NP. Further research will be done to determine the exact surface chemistry of OA on the AZO-NP.

6. References

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