

1. Introduction

In the field of light-emitting devices, solar cells and photodetectors, inorganic colloidal nanoparticles are very promising because of their interesting physical and chemical properties. One drawback of these materials is that in order to keep them stable in solution they need to be stabilized with surface ligands. These surface ligands are for example molecules with long hydrocarbon chains (C8-C18). As a result, the nanoparticles are surrounded by a highly insulating barrier that makes their use in above devices problematic. One way of getting rid of this problem is exchanging these long ligands with shorter ones or with inorganic molecules such as molecular Metal Chalcogenide Complexes (MCCs). They keep the nanoparticles stabilized in the colloid and enable strong electronic coupling. An interesting MCC ligand is for example Sn₂S₆⁴⁻. However, when this MCC solution is synthesized, also other Sn-complexes (f.e. SnS₄⁴⁻) can be formed. The lack of hydrogen atoms in these systems makes them challenging to characterize, moreover, literature concerning these systems is scarce. Using ¹¹⁹Sn NMR we attempted a full characterization of the solutions of MCC complexes as synthesized.

2. Materials and methods

Synthesis of the complexes was carried out by dissolving SnS₂ in aqueous (NH₄)₂S at pH 14. NMR samples were prepared with 10% D₂O. Measurements were recorded on a Bruker 700 MHz AVANCE II spectrometer and a Bruker 500 MHz AVANCE II spectrometer at ambient temperature. ¹¹⁹Sn measurements were recorded with proton decoupling during acquisition.

3. Measurements as a function of pH

A series of measurements was performed adjusting the pH from 14 gradually to 8.5 by addition of HCl. pH values lower than 8.5 could not be achieved because the suspension precipitates when doing so, most probably due to the formation of MCC polymer chains.

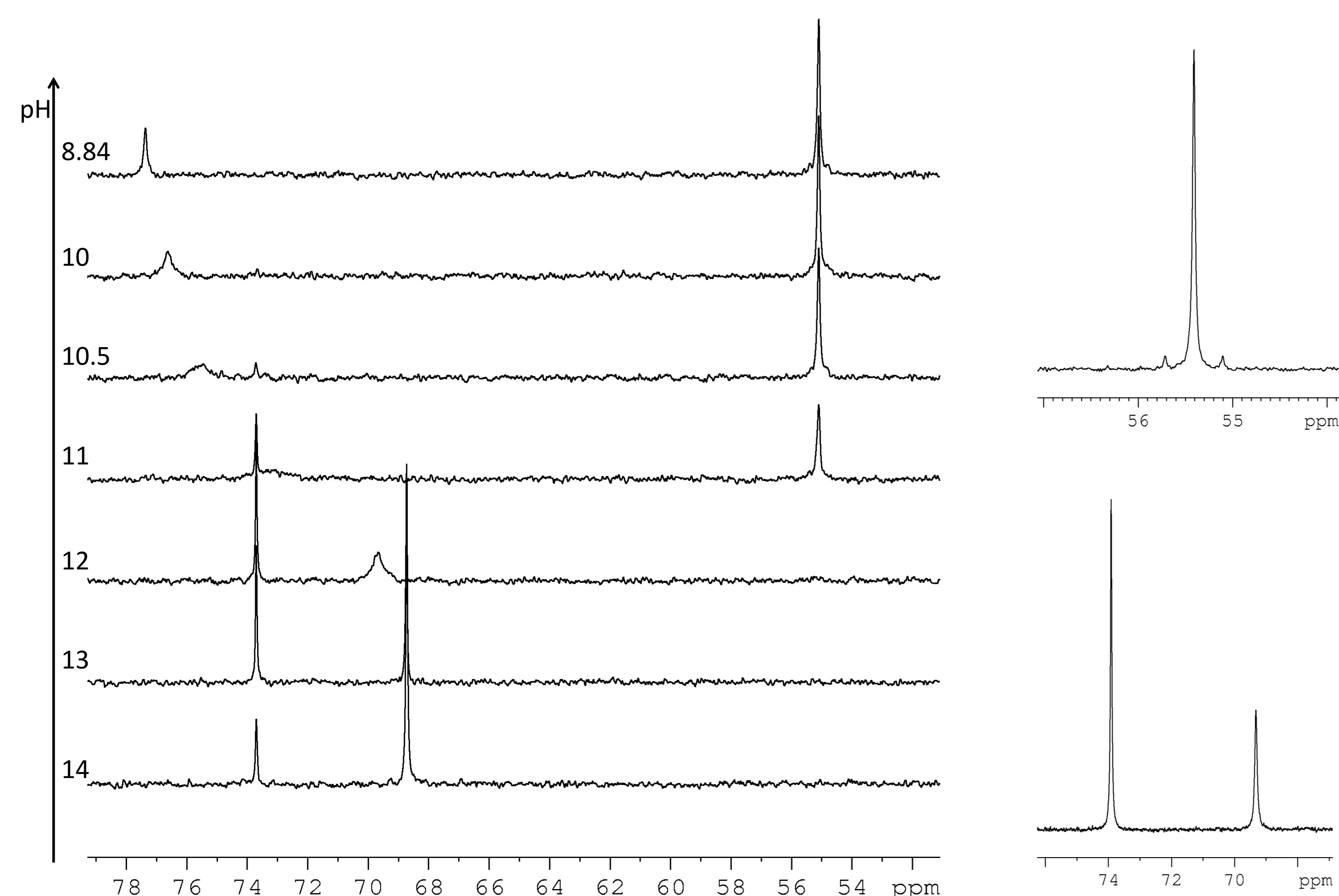


Figure 1. left: ¹¹⁹Sn spectrum at 186.5 MHz of a solution of MCC in D₂O at different pH and 25°C. Chemical shifts were referenced against external TMSn. Right: long measurement of different species to visualize satellite peaks.

During these experiments four species are visible. The one at 55.4 ppm appears only below pH 12 and increases with decreasing pH. The one at 74 ppm first increases, and then decreases with decreasing pH, disappearing from pH 10 downwards. Both appear at fixed frequency and line-width. Two species appear to be in intermediate to fast exchange, demonstrating an equilibrium that shifts with pH. From literature¹ we can expect the signal at 55 ppm to be Sn₂S₆⁴⁻. Indeed, if we look at the satellite peaks these both have an integration of 4.3 % of the main signal. This is what we expect for the given complex because Sn has two main NMR active isotopes ¹¹⁹Sn and ¹¹⁷Sn, meaning that in the Sn₂S₆ molecule there should be a certain amount of ¹¹⁹Sn-S-¹¹⁷Sn isotopomer. The other signals don't have visible satellite peaks. From literature and previous studies, we might expect the signal at 74 ppm to be SnS₄⁴⁻. The chemical shift evolution of the species in equilibrium, further referred to as Sn_x and Sn_y, is shown in figure 2. By taking the derivative of the graph the pK can be estimated to be around 10.5.

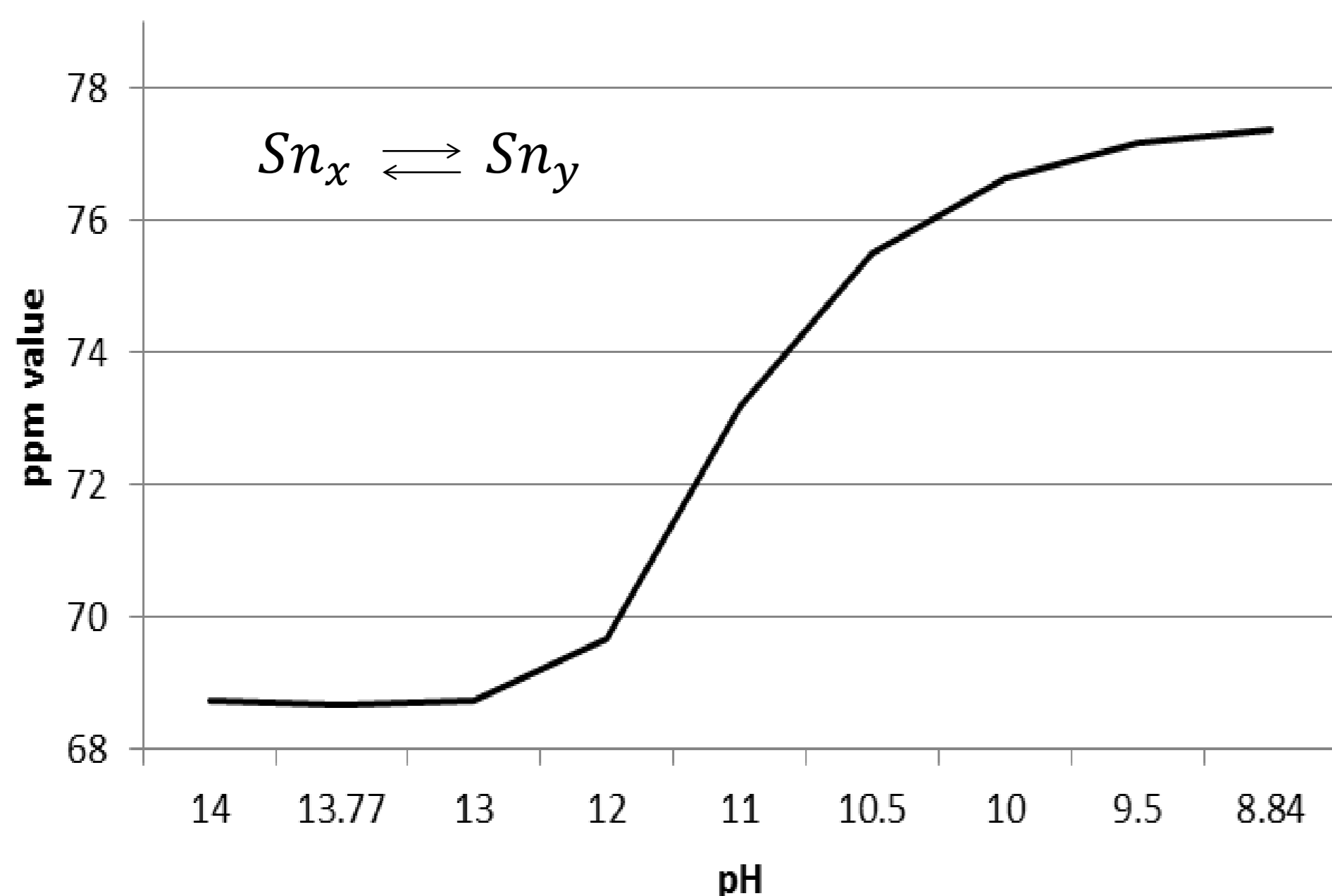


Figure 2. Graph of the change in chemical shift value as a function of pH for the exchanging species

In figure 3 the dependence is shown between the fraction of two species in fast exchange and the line width. This is in good agreement with what we observe in the series of pH measurements. One peak that is sharp, decreases, shifts and broadens, to sharpen up again afterwards.

$$\delta_x = x\delta_{Sn_x} + (1-x)\delta_{Sn_y}$$

$$\frac{1}{T_{2,obs}} = \frac{x}{T_{2,Sn_x}} + \frac{(1-x)}{T_{2,Sn_y}} + \frac{x(1-x)^2(\delta_{Sn_x} - \delta_{Sn_y})^2}{k_{-1}}$$

Figure 3. fast exchange and the influence on the line width.

4. Study on equilibrium between Sn_x and Sn_y

To study the equilibrium, a dilution experiment was performed. The sample is diluted to half the concentration while the pH was kept constant during this experiment. ¹¹⁹Sn spectra of these samples are shown in figure 4. Diluting the sample to half the concentration shifts the equilibrium to the right.

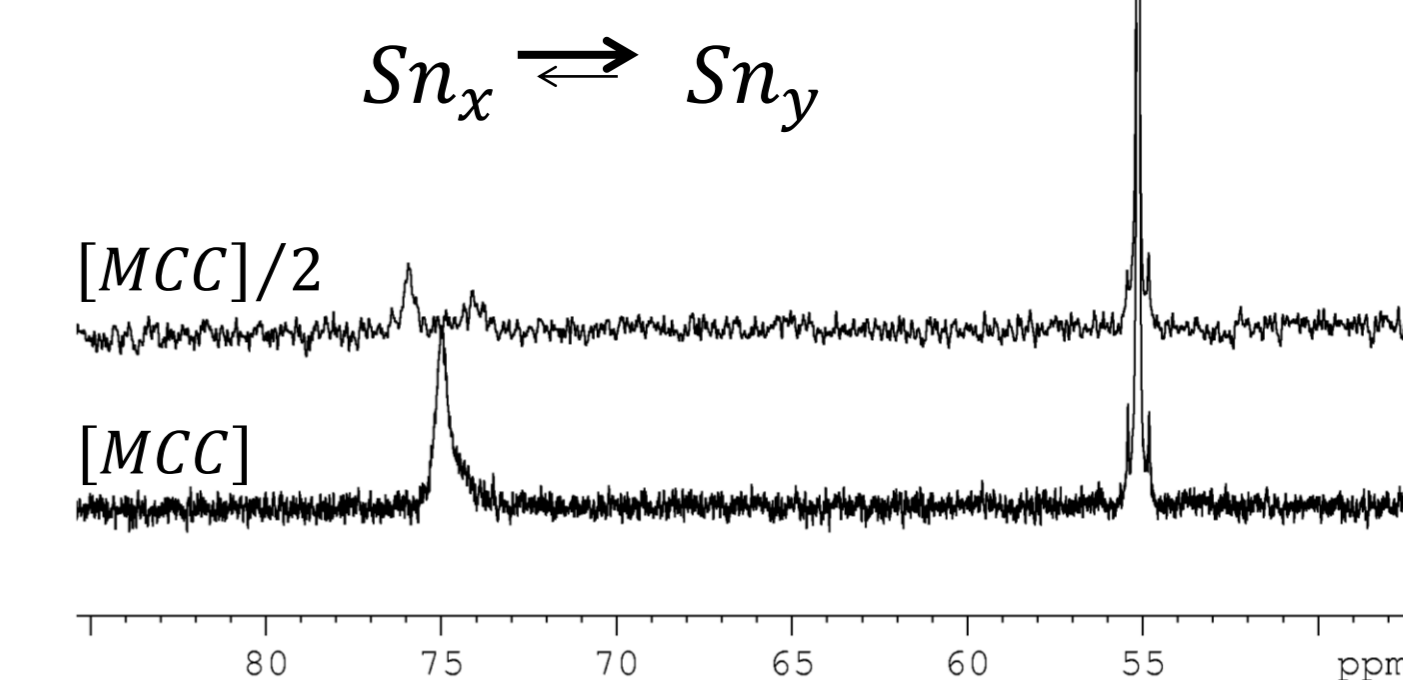


Figure 4. ¹¹⁹Sn spectra of the MCC sample at pH 10.9 before and after dilution.

5. Measurements as a function of temperature

The sample at pH 12.7 was measured at 4 different temperatures to study the influence of temperature on the equilibria in the MCC solution. The temperatures chosen were 278 K, 298 K, 313 K and 333 K. Both signals shift to the right and decrease in intensity when increasing temperature, figure 5. The signal at 69 ppm decreases and broadens more rapidly than the signal at 73 ppm which however also broadens at higher temperature.

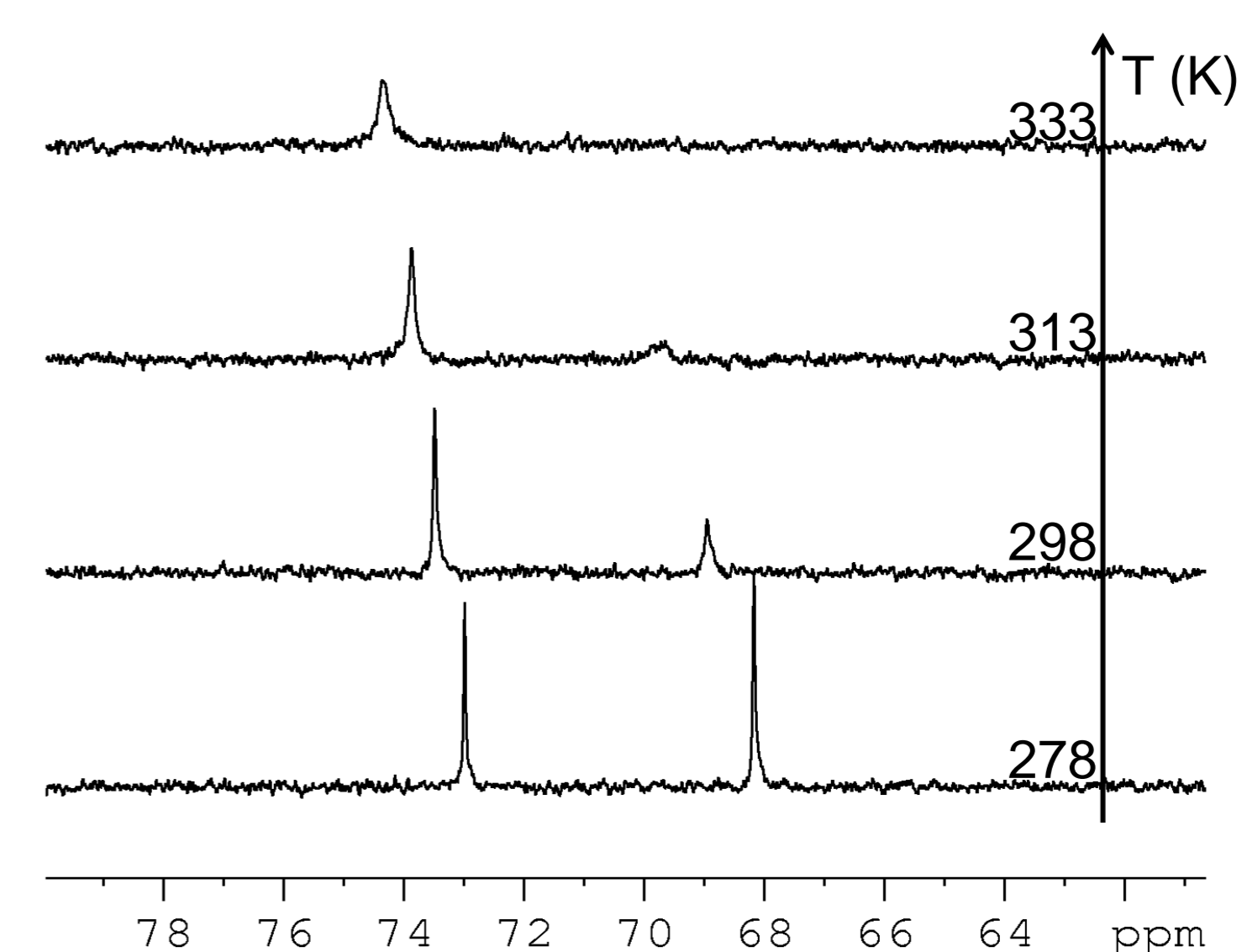


Figure 5. ¹¹⁹Sn spectra of the MCC sample at pH 12.7 at different temperatures.

6. Future prospects

In the future, assignment of the different peaks will be performed completely. Now we have an idea of two out of four peaks but also the observed equilibrium should be assigned. At first we assumed none of the species would contain proton but with the observed equilibrium, this might well be the case. A ¹H 1D and ¹¹⁹Sn without decoupling will be recorded to check if there are indeed no protons present in the species.

7. References

[1] Kovalenko, M. V., M. Scheele, et al. (2009). *Science* **324**(5933): 1417-1420.