High Resolution NMR of water in single-wall carbon nanotubes

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Introduction

Recently there has been much interest in the structure of water in confined spaces. Computer simulations suggest that water in carbon nanotubes can form one-dimensional polymorphs of ice nanotubes.

Here we report NMR investigations of (liquid) water in single wall carbon nanotubes (SWCNTs). By using magic angle spinning more than one water resonance of water in such materials is detected. These different resonances show different freezing behavior and are attributed to water absorbed inside and outside the nanotubes. The experiments confirm that the first water that is absorbed by carbon nanotube material is absorbed in the nanopores.

Experimental

SWCNTs were produced by catalytic conversion of high-pressure CO over Fe particles (HipCO process) at CNI in Houston. The raw samples were stepwise purified by controlled thermal oxidation in air, followed by a HCl treatment. This has led to samples with an average tube diameter of 1.0 nm and decreasing amounts of Fe impurity. The NMR experiments were carried out on a Bruker Avance 400 MHz spectrometer with samples rotating at the magic angle at 3250 Hz in a 4 mm zirconia rotor.

Results

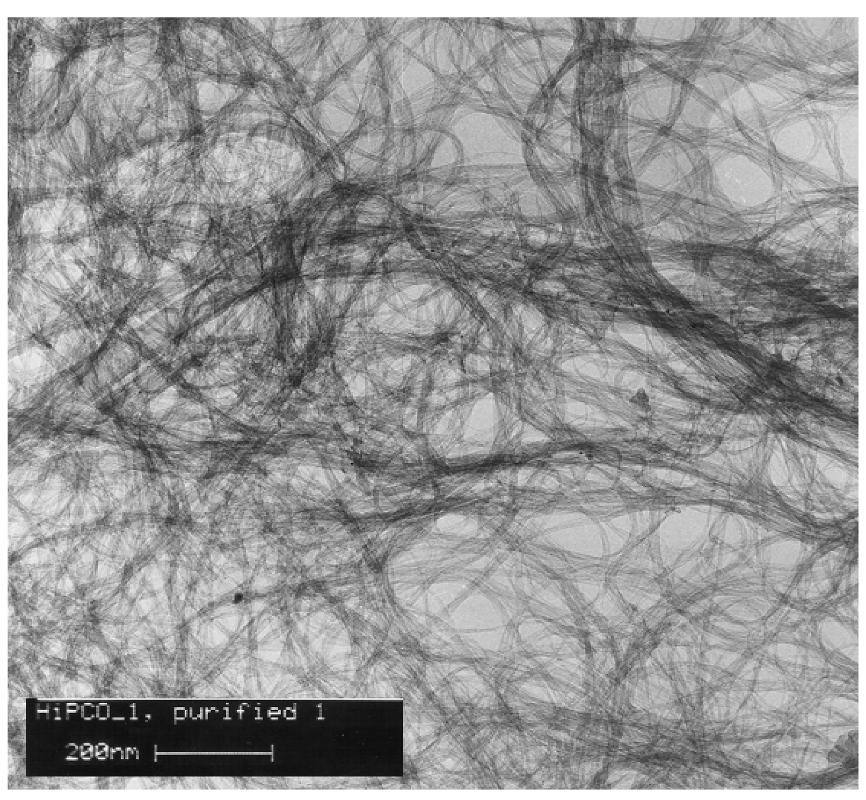

Fig. 1 TEM pictures of purified SWCNTs

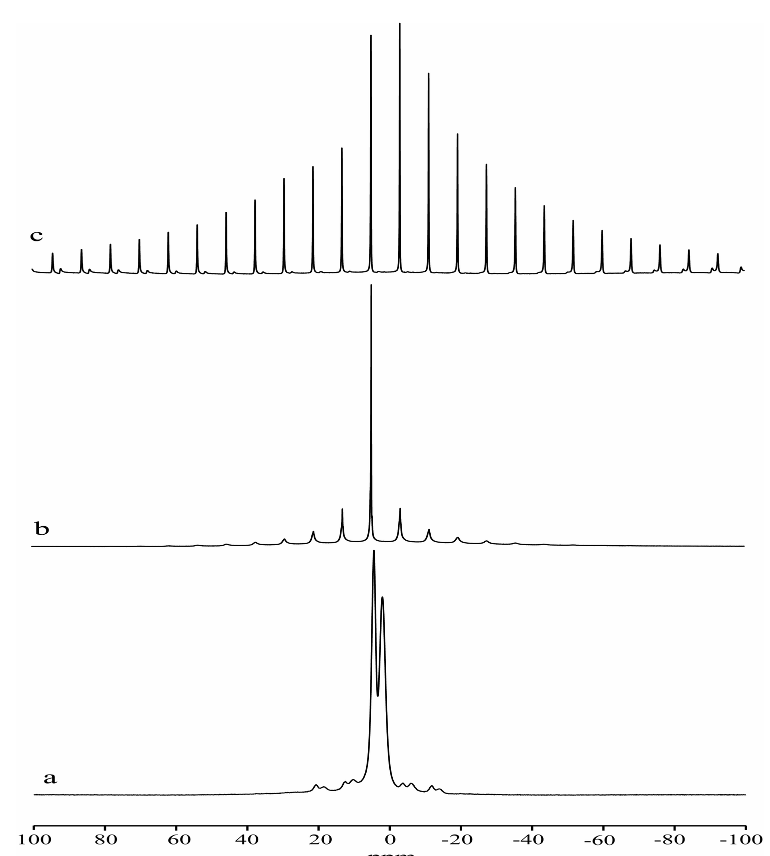

Fig. 2 1H MAS NMR spectra of water as a function of the Fe concentration at 250 wt% water

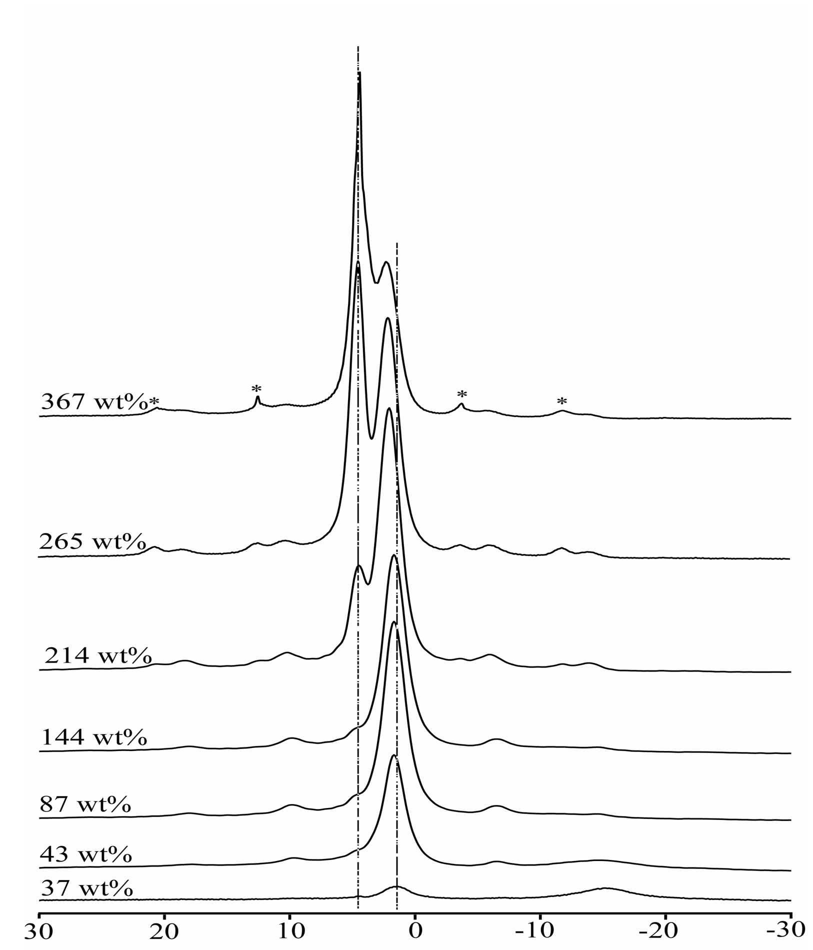

Fig. 3 1H MAS NMR spectra of water In SWCNTs as a function of the wt% water

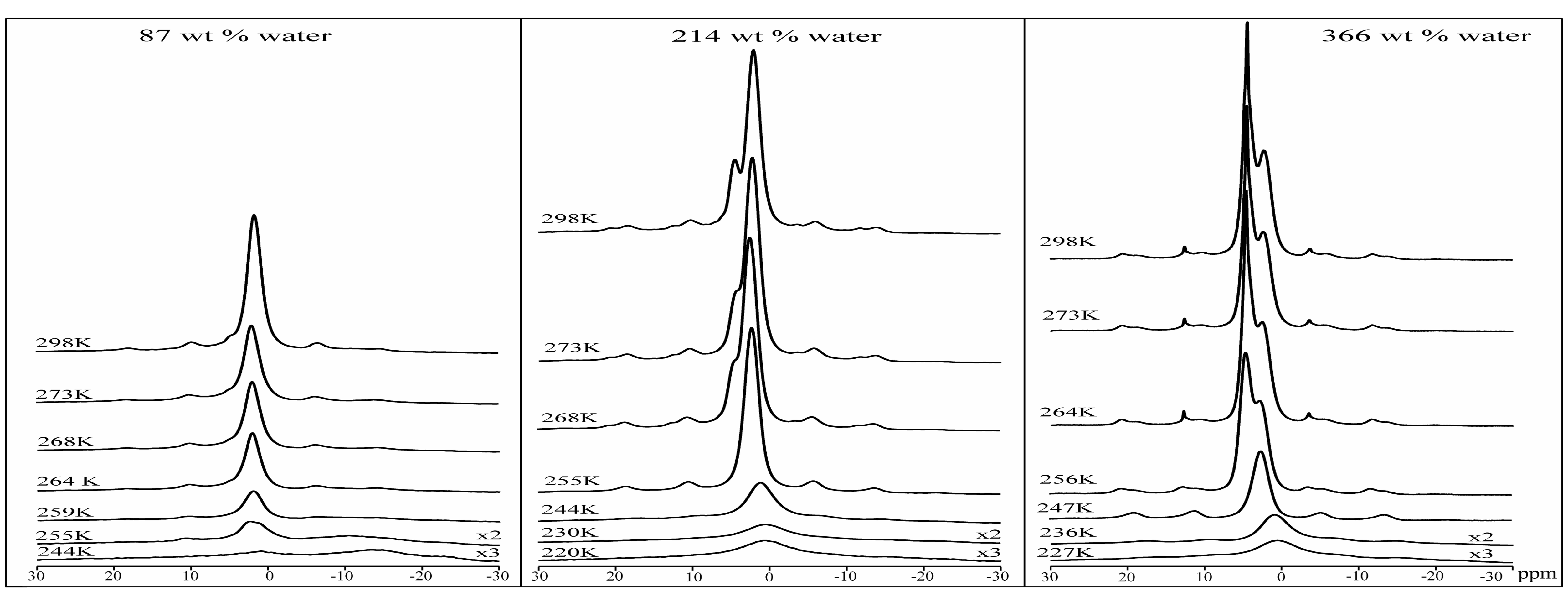

Fig. 4 1H MAS NMR spectra of water in SWCNTs as a function of temperature at three different water loadings

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Discussion

Fig. 2 makes clear that for NMR experiments of water in SWCNTs it is important to remove as much of the magnetic Fe catalyst as possible. At high Fe concentrations the water NMR lines broaden. Although magic angle spinning breaks up the broad line into spinning sidebands, some of the broadening remains.

Fig. 3 shows that at the lowest water loading two resonances are found at 1.3 and -15 ppm. Upon increased water content an additional line appears at 4.6 ppm. At very high water loadings this line overwhelms the other two lines.

Fig. 4 demonstrates the temperature dependence of the resonances for three different loadings. Here it is important to realize that our NMR technique is only sensitive to liquid water, i.e. as soon as the water turns into (one-dimensional?) ice, the line disappears due to excessive broadening. This figure proves that the first water that is absorbed into the SWCNTs, which resonates at 1.3 ppm, freezes at 220-240 K. The water that resonates at 4.6 ppm freezes at 255-264K.

Conclusion

From the water concentration and temperature dependence of the NMR spectra we conclude that the line at 1.3 ppm is from water inside the 1 nm nanopores and that the water responsible for the 4.6 ppm line is adsorbed at the outside of the (bundles of) nanotubes. Simple model calculations show that the difference in chemical shift is due to the shielding of the magnetic field by the carbon frame of the tubes.