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Tuning the Properties of Confined Water in Standard and Hybrid Nanotubes: an Infrared Spectroscopic Study

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Imogolite is a natural nanotubular aluminum silicate clay mineral, originally found in volcanic soils. Its well-defined, yet tunable structure makes it a good candidate for the study of water confined in a one-dimensional structure. Water confined in imogolite self-sustaining thin films was studied by means of infrared spectroscopy [1]. Two types of synthetic imogolites were investigated: a pristine imogolite (IMO-OH) with a hydrophilic inner surface fully covered with Si-OH groups and a hybrid imogolite (IMO-CH₃) with a hydrophobic inner surface fully covered with Si-CH₃ groups. Both imogolites have the same outer surface, covered with Al-OH groups. The infrared spectra were recorded in the 20 - 4000 cm⁻¹ spectral range as a function of the relative humidity. In particular, a detailed analysis of the O-H stretching band provides information on the H-bonding of confined water molecules inside and outside the IMO-OH tubes. The analysis of the various infrared signatures reveals the scenario for water filling as a function of relative humidity for the two systems. The adsorption in the IMO-OH tubes starts at the lowest relative humidity (< 10%). The inner surface of the tubes is first covered with water molecules, followed by the filling-up of the central part of the tubes, leading to very strong H-bonds and a structured spectrum. In contrast, the H-bonds of water adsorbed at the outer surfaces of these tubes are weaker. A different scenario is evidenced for water inside IMO-CH₃: very weakly H-bonded water molecules are present, a situation similar to what has been observed in carbon nanotubes. The present work shows that water confinement in imogolites is governed by the hydrophilicity of the inner walls. Indeed, at similar partial pressure, water can be less or more H-bonded depending on its interactions with the nanotube wall [2].

[1] Y-Y. Liao, P. Picot, J.-B. Brubach, P. Roy, S. Le Caër and A. Thill, Self-supporting thin films of imogolite and inogolite-like nanotubes for infrared spectroscopy, *Appl. Clay. Sci.* (2017), <https://doi.org/10.1016/j.clay.2017.1006.1005>

[2] Y-Y. Liao, P. Picot, M. Lainé, J.-B. Brubach, P. Roy, A. Thill and S. Le Caër, Tuning the Properties of Confined Water in Standard and Hybrid Nanotubes: an Infrared Spectroscopic Study, *Nano Research*, in press.