Water- and Calcium-Bridges in Nanopores of Humic Acid Models: Static DFT and Dynamic DFTB Investigations

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Humic substances (HS) play an important role for the adsorption process in soils being key agents in determining the fate of pollutants such as pesticides. Due to the flexibility of HS various nano pores and holes can be formed in their structure. Water molecules can establish a stable network of hydrogen bonds within these structural units that can be viewed as “wet spots”. Thermal analysis and proton NMR relaxation show the importance of intermolecular crosslinks via bridges of water molecules.

In this contribution the polar functionality of HS is modeled by carboxyl groups aligned along an acrylic acid trimer chain or by singly carboxyl groups attached to the ends of aliphatic chains. The figure shows the interaction of two such trimer chains (side view and top view) with water molecules as linking modules. DFT optimizations and DFTB dynamics simulations have been performed to determine the thermodynamic stabilities of these aggregates. Additionally, the stabilizing effect of Ca^{2+} bridges between carboxylate groups is discussed for varying water content.