



Molecular Modelling of Water Adsorption on Hydrophobic and Hydrophilic Self-assembled Monolayers as Proxies for Atmospheric Organic Surfaces

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Organic compounds present in atmospheric aerosols throughout the troposphere may alter the hygroscopic and cloud nucleating properties of aerosols. Understanding of the water uptake behaviour of organic-containing particles is one of the essential steps towards accurate modeling of various phenomena from visibility to cloud effects and climate forcing by tropospheric aerosol. Self-assembled monolayers (SAMs) of functionalized alkanethiols on gold are among the proxies that are currently being used to study the properties of atmospheric organic surfaces in a variety of laboratory experiments. The well-defined character of SAMs gives us control of the surface structure and chemical functionality so we can study how those aspects of a surface influence the water – surface interaction.

Over the recent years, molecular dynamics (MD) simulations have become increasingly useful in providing insight on a molecular level into the processes occurring at atmospheric surfaces. The principle aim of this study is to explore how the order, molecular structure, chemical functionality and the hydrogen-bonding nature of organic surfaces affect their interaction with water. The MD simulations are used to identify the important molecular factors that control water uptake on organic surfaces at various stages of their processing in the atmosphere.

This study focused on water interaction with single-component SAMs of different functionality (e.g. methyl terminated C8 SAM, carboxylic acid terminated C8 SAM) as well as with SAMs comprised of multi-component mixtures (e.g. mixed methyl terminated C8 / carboxylic acid terminated C4 SAM). For the saturated SAM, clear depletion in the density of water close to the water-SAM interface is observed. As a consequence of the stronger water-water interaction compared to the water-hydrophobic SAM surface interaction, the de-wetting transition occurs in several trajectories when water, initially wetting the entire SAM, forms islands or droplets on the surface and leaves parts of the SAM surface exposed. In the case of the oxidized ($-\text{COOH}$ terminated) SAM, water molecules are in direct van der Waals contact with the SAM surface and no near-surface depletion of the water density is observed. The formation of $-\text{COOH}$ dimers and the change in the hydrogen-bonding pattern between the $-\text{COOH}$ end-groups caused by the surface-adsorbed water are analyzed. Of particular interest is whether water uptake will be enhanced in the pores of corrugated surfaces formed by a mixture of SAMs as illustrated below. Both water-hydrophobic and water-hydrophilic interaction effects are present for the mixed SAM, with water penetrating into the hydrophilic pore within the hydrophobic surface. The results of these MD simulations provide a valuable insight into molecular aspects of water interaction with organic surfaces and help interpreting the related experiments.