

Effects of surfactants in heterogeneous formation of aerosols on soluble organics

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Atmospheric organic and bio-aerosols have long been known for their ability to serve as active cloud condensation nuclei (CCN) and ice formation nuclei. Although local (e. g., toxicity, health hazards) and global (e. g., climate change) impacts of such aerosols are suspected, the significance of organic molecules in driving physico-chemical atmospheric processes is highly uncertain owing to the complex chemical nature of such molecules. Also the formation pathways of organic aerosols are poorly understood. Recently, Sun and Ariya (2006) published a comprehensive review to assess the current state of knowledge about the role of organic aerosols as CCN.

Previous field observations reveal the widespread occurrence of mixed organic and inorganic species within the same atmospheric particle. With respect to their morphology these mixed aerosols are formed by coating of both continental and marine inorganic aerosols (sea salt, dust, sulphate) with organic films. The organic films mainly consist of fatty acids, originating from different anthropogenic and natural emission sources (e. g., biomass burning, exhalations from the ocean), with the carbon chain lengths depending on continental or marine origin of the inorganic aerosol (Sun and Ariya, 2006).

Fatty acids belong to the so-called surfactants (surface active agents). Surfactants are usually amphiphilic compounds, i.e., they contain both hydrophilic head groups of molecules and hydrophobic (or lipophilic) tail groups, enabling their solubility in both organic solvents and water.

There are several effects of soluble surfactants in thermodynamics of heterogeneous nucleation of water vapour. Surfactant molecules are able to accumulate at the liquid-vapour interface of water solutions forming a surfactant monolayer. This effect leads to two important consequences: first, the surface tension of water can be considerably reduced by 2 or 2.5 times, and second, the decrease of bulk surfactant concentration due to repartition between surface and bulk of a droplet shifts its chemical equilibrium. As a result, the Kohler theory of nucleation on soluble particles requires reconsideration in the case of surfactant particles in order to take into account these adsorption and material balance effects (Shchekin et al, 1995, 2002; Sorjamaa et al, 2004).

Above a certain concentration of monomeric surfactant molecules in a bulk solution, surfactants begin to assemble into aggregates, so-called micelles. The threshold concentration is denoted as critical micelle concentration (CMC). Micelles can be formed as spheres, ellipsoids, cylinders and bilayers, whereas the shape and size are functions of the molecular geometry of their surfactant molecules and solution conditions (e. g., surfactant concentration, temperature, pH, and ionic strength). Depending on the polarity of the head group one can distinguish four primary groups of surfactants: anionic, cationic, non-ionic and zwitterionic.

Aggregation of micelles, or micellisation, should affect atmospheric nucleation and aerosol formation (Tabazadeh, 2005; Graber and Rudich, 2006). First attempt here was done by Shchekin et al (1993) with using the phenomenological parametrization of micelles and their CMC. The present communication adopts a thermodynamic and kinetic approach to micellisation, recently proposed by Shchekin et al. (2005), which allow us directly calculated the aerosol micellisation parameters required in nucleation theory.

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