

Surfactants in cloud activation: do they matter?

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It has been recognized for nearly two decades that the surface tension of aqueous aerosols will play a critical role in governing their cloud forming abilities (Shulman, 1996) and that surface active compounds with the potential to substantially decrease surface tension are indeed present in atmospheric aerosols (Facchini, 1999).

Decreased surface tension at the point of droplet activation is readily anticipated from standard Köhler theory to enhance cloud condensation nucleus (CCN) potential. Increased CCN activity may in turn influence the aerosol indirect climate effects via cloud droplet numbers and sizes, and hence cloud albedo and life time. This makes surfactant components an alluring unicorn for reconciling measurements with predictions of atmospheric CCN.

Nevertheless, after a good many studies of surfactant CCN activity and several important insights as to the influences of surface activity on droplet activation thermodynamics, the overall impact of surface active aerosol components on CCN activity and large scale aerosol climate effects remains ambiguous. In some cases, enhanced aerosol CCN activity has been rationalized with considerations of reduced aqueous surface tension by surface active organic components (Asa-Awuku, 2008), whereas other studies have shown that the overall effect of surfactants on CCN activation is nearly negligible (Prisle, 2011).

Many different factors contribute to this bothersome dilemma. We highlight some of these and the mechanisms by which studies of CCN activity are impacted. The first question is what the surface tension of aerosols actually *is*? It cannot be measured directly. Surfactants accumulate at the aqueous surface and the resulting partitioning of dissolved material between bulk and surface phases may deplete the bulk in small droplets with large surface areas. This can affect the surface tension and thus the curvature effect on equilibrium vapour pressure of activating droplets, and may greatly change the solute effect (Sorjamaa, 2004).

When you want to model the global effects of surfactants in atmospheric aerosols, detailed process level descriptions are too complex to be readily implemented in large-scale frameworks (Kokkola, 2006). Furthermore, the non-linearity of surfactant effects in activation thermodynamics challenges attempts to parameterize process level mechanisms over an aerosol population of different sizes and compositions (Prisle, 2011, and references herein).

A number of recent studies measure and parameterize surface tensions of atmospherically relevant aqueous systems as functions of varying composition. Such surface tension measurements and

parameterizations are essential for including surface tension effects in modelling of droplet activation. Still, it is futile to ever hope of getting a comprehensive description of surface tensions over the entire range of aqueous mixing states found in atmospheric aerosols. The surface tension of solutions comprising known atmospheric surfactants has been seen to respond to mixing with other solutes in ways that are not readily anticipated. Surface tension measurements may frequently have been performed for mixing states not representative of atmospheric aerosols, thus decreasing the usefulness of the derived parameterizations. Furthermore, the first studies of global climate effects resulting from surfactant CCN activity points to the need for great caution when representing the ensemble of surface active organic aerosol by simple proxy systems (Prisle, 2012a).

It was recently shown that atmospheric surfactants are not chemically inert, but rather may participate in chemical reactions in the aqueous surface. Such reactions may consequently alter the surface composition and properties, and may even occur without corresponding changes in the bulk solution taking place (Prisle, 2012b).

We revisit results from previous studies of aqueous surface tensions for atmospherically relevant aerosol mixtures and their effects on predicted CCN activity. We wish to guide and focus future efforts targeting effects of surface active atmospheric aerosol, such as for which aqueous systems, and in particular which compositions and concentrations, to measure surface tensions. We explore simple frameworks within which to assess implications of measured surface tensions for CCN activity of aqueous aerosols, ultimately to make recommendations for the treatment of the different properties of surfactants in large scale modelling of aerosol climate effects.

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