**Atmospheric
Chemistry
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Discussions**

Interactive
Comment

Interactive comment on "A simple representation of surface active organic aerosol in cloud droplet formation" *by* N. L. Prisle et al.

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1   Response to Anonymous Referee # 1:

(A) I don't really understand why total surface partitioning is not affecting the surface tension of the systems. Fig. 1d shows an effect of 5-10%. Or is such an effect regarded as not significant (p. 23611).

The surface tension is unaffected by the presence of surfactant in the case of total surface partitioning as a consequence of describing surface phase properties, here the surface tension, in terms of bulk phase composition, as must be valid at equilibrium between the two phases. The complete partitioning of surfactant molecules

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to the surface implies a corresponding vanishing bulk concentration, which upon substitution into a concentration-dependent surface tension parametrization in turn results in a vanishing surface tension reduction. This is of course under the additional assumption that only the surfactant solute affects solution surface tension according to the parametrization used, that is, any influence of the inorganic salt solute (intrinsic or via organic-inorganic interactions) on surface tension is disregarded. This is explained in detail in Section 2.4 of the manuscript, and we have made slight modifications to further clarify this important point.

The referee has a very good point that, in case of the example shown in Fig. 1d, a 5-10% decrease in droplet surface tension is indeed predicted at the point of activation, and for the purpose of the simple representation presented here, this effect is disregarded altogether by neglecting any surface tension reduction within the activating droplets. The example shown may well represent a maximum effect for the cases studied, in terms of surface tension reduction attained at the point of droplet activation, and in either case the droplet surface tension is reduced much less than would be anticipated from the total surfactant concentration in the droplets. Furthermore, because of several mutually connected effects, this total surfactant concentration remaining in the droplet bulk phase at the point of activation is not readily anticipated and requires complex calculations and numerical solutions to the surfactant bulk-surface partitioning equilibrium and the droplet water vapor pressure equilibrium. Therefore, as a first order approximation, the surface tension reduction from the surfactant is disregarded altogether when predicting the droplet activation properties within the simple representation presented here. The detailed thermodynamic modeling of Prisle et al. (ACP, 2010) shows that, for the particle compositions investigated here, the effect of any surface tension reduction on predicted droplet critical supersaturation is dominated by the effect of diminished solute effect from bulk-phase depletion of surfactant molecules. We have made slight modifications to further clarify this point in the revised manuscript.

(B) In the authors earlier work (Prisle et al. GRL, 2010) they consider phase separation in an organic and an aqueous phase in mixed SOA/inorganic salt particles as one option. This would be in accordance with findings e.g. by Anttila et al. (J. Atm. Chem. 2007), who observed formation of SOA coatings on aqueous particles. Would such particles with two phases / coated particles be covered by the simplified approach?

This is an excellent point. Complete surface partitioning, as assumed by the simple representation presented here, is merely one form of organic separation from the aqueous phase. In principle, any form of organic phase separation from the activating aqueous solution droplet is covered by the simple representation, by which the only contribution of the organic aerosol fraction is to the overall surface curvature of the activating CCN. It must however be emphasized that the simple representation only pertains to describe the overall CCN activity of the organic aerosol fraction, that is, it describes just one property of the aqueous droplets, and only at the point of droplet activation. It is thus implied that the separate organic phase, whether a solid core, an immersed liquid bulk phase, or an organic coating on the aqueous droplet surface, does not itself have any CCN potential (by not interacting with the aqueous phase and thus affecting its surface tension and/or solute effect) and does not inhibit the equilibrium mass transfer of water vapor to/from the activating aqueous droplet phase.

(C) The conclusions about the applicability to atmospheric systems it is a bit optimistic. It is likely that the organic fraction in atmospheric aerosols is not be overall composed of surfactants. Then the simplified representation would only work if we would be able to determine the soluble and the surfactant fraction. The problem is then

shifted to determine this fraction and for the soluble fraction we are still be left with all problems as before. Nevertheless, this can be investigated in the lab as proposed by the authors. It would be helpful if the authors would comment in the conclusion section if and where they see likely applications for atmospheric particles (marine particles with biological material picked up from the ocean surface?).

This is another good point, that we have taken note of. We certainly do not mean that all organic aerosol in the atmosphere (measured or modeled) is likely to be represented by the properties of a strong surfactant. We aim to highlight that because the simple representation presented here does not require knowledge of the composition and molecular properties of the organic fraction, and because it is computationally very simple, it has potential applications for describing complex and realistic aerosols, and for implementations in large scale models describing the cloud microphysics of such aerosols. It is naturally only applicable to aerosols where the organic fraction can be properly represented by the assumed surface active characteristics. We have made slight revisions to the text in order to clarify this point.

Of course, in the atmosphere, not all organic aerosol is composed of strong surfactant. The extent of organic surface activity that can be properly described in calculations of CCN activation by the presented simple representation needs to be investigated further, just as the scope of this representation in terms of the applicable range of mixing states with both different organics and inorganics. This calls for comparison to extensive laboratory and ambient measurements, and is the focus of ongoing work. The presented simple representation is a first order solution to describing the CCN activity of surface organics and is seen to work well for the aerosol compositions presented here, with relatively strong atmospherically relevant organic surfactants. These specific compositions can be regarded as simplified two-component model systems for marine aerosol (Prisle et al., ACP, 2010, and references therein), as also suggested by the referee.

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Interactive Discussion

Discussion Paper

As a next step in elaborating the representation of CCN potential for the organic aerosol fraction, the description could be split into a linear combination of two contributions, namely those of a strong surfactant and a fully soluble (and thus non-surface active) fraction, as also suggested by the referee. The strong surfactant fraction could then be described by the present simple representation, and the soluble fraction for example by a single overall hygroscopicity value. As the referee points out, the problem is then shifted to determining the distribution of the organic aerosol phase between these two discrete regimes. However, with this linear combination of properties, a considerable simplification is actually achieved for the soluble organic fraction, by essentially removing the uncertain contribution of surface tension effects to the resulting hygroscopicity. Representing organic aerosol CCN activity by such a linear combination of properties from two discrete fractions, and thus with essentially two parameters (the surfactant-soluble distribution factor and a single hygroscopicity value for the soluble fraction) is still feasible in large scale modeling, and is in principle still measurable with available techniques for complex/unknown organic aerosol compositions. Thus, this representation has the same fundamental characteristics as the very simplest approach introduced here, while providing the next level of complexity in describing organic aerosol CCN properties. This next order representation will be the focus of future work.

(D) p. 23606. Isn't the "solubility product" a constant for a given solute? I think what is meant here is that common ions in the solution lead to exceeding the solubility product of the surfactant.

This is correct. Indeed, the solubility product is a constant. What is meant is that the contribution of organic anions originating from dissolved surfactant to the solubility product is decreased in the presence of inorganic salt with a common anion

in the droplet solution. We have corrected the text accordingly.

(E) Fig. 1 Caption b) appears twice.

This has been corrected.

2 Response to Anonymous Referee # 2:

(F) Page 23603. The authors state that the combined effect of surface partitioning and surface tension effects is not readily anticipated in each case. This is quite an important point with regards to 1) the often unfortunate drive to neglect even 'low' levels of cpmplexity and 2) the need for schemes such as the one presented here. I do wonder however whether this demands that one has to have domain based parameterisations. How would one, for example, provide a scheme for different environments and would the level of simplification proivided be able to capture the dynamic evolution of the aerosol properties(i.e. surfactant 'nature')? Along these lines of discussion, is it not pertinent to assume the organic fraction to be described by at least a low order collection of different typres of surfactant? Or do the auhthors believe can we assume the organic fraction to be accurately modelled essentially using one isotherm to represent the complex mixture?

This comment contains several important points. First of all, the presented simple representation of surface active organic aerosol CCN activity provides the simplest possible, or first order, level of complexity in such a description, as explained in point (C). Assuming complete surface partitioning of all organics within the activating droplets represents one extreme end of properties in terms of the influence of surface activity on organic aerosol CCN potential. As such, by essentially describing one

single (end) point of the combined surface partitioning and surface tension effects on the CCN activity isotherm, this representation is not capable of capturing any variation in CCN activity with changing organic aerosol composition, let alone the dynamic evolution of CCN properties due to such changes within an aerosol population.

By providing the lowest possible level of complexity, conceptually and computationally, in a description of the combined effects of surfactant properties on organic aerosol CCN activity, the proposed simple representation in turn provides the entry point for testing the significance of these effects in large scale atmospheric modeling. Before elaborating on the representation of surface active organic aerosol CCN activity, there is a need to study the potential atmospheric relevance of such surfactant effects, in terms of surface partitioning and surface tension reduction, and the necessary level of accuracy needed to model atmospheric surfactant CCN properties adequately. Of course, the required level of accuracy depends on what is studied. For instance, if one studies the relevance of surfactants on global cloud properties, the computational burden in describing the effect of surface activity on cloud activation must be kept to the minimum. In such a study, the surfactant types could for example be divided according to the emission source environment. Nevertheless, the knowledge of the chemical composition and physical properties of surfactants that are abundant in the atmosphere is still fairly low, so this would be a difficult task on its own. The method presented in our study would therefore suit global scale studies well, since the cloud activation can here be calculated without knowledge of the surfactant molecular composition and properties.

Surface activity has been widely demonstrated in atmospheric aerosol samples from a wide variety of environments (Prisle et al., ACP, 2010, and references therein). Still, it is indeed unlikely that all organic aerosol found in the atmosphere or produced in laboratory smog chamber experiments is surface active, let alone composed solely of a mixture of strong surfactants. We therefore do not propose that this simplest

representation will capture the CCN properties of all kinds of organic aerosol, in any mixing state and in any ambient conditions. As explained in point (C) above, the specific aerosol systems studied here are representative of marine aerosol (Prisle et al., ACP, 2010, and references therein), yet the extent of applicability of the proposed representation needs to be investigated further, and is the focus of ongoing research.

As also explained above, the level of complexity of the presented representation of organic CCN activity can however be expanded within the framework provided here, with little additional computational complexity. As a next order representation, the organic CCN potential can be described by linear combination of a surface active and a non-surface active hygroscopic organic aerosol fraction, respectively. The description of the surface active fraction can subsequently be expanded into a linear combination of a range of resulting surfactant effects on CCN activity. As soon as the surfactant effects on CCN activity are expanded into (even the simplest) linear combination, it also opens possibilities for capturing some level of dynamic evolution. However, due in particular to the lack of experimental data for reference, it is currently difficult to establish the validity of such (a) representation(s).

(G) Page 23614. The authors breifly discuss the applicability of parameterisations based on the expected composition and inorganic:organic ratios found in the atmosphere and comparisons with laboratory data. It would appear the labratory comparisons all include inorganic/organic systems with a common ion (Na). It has been shown that these system can exhibit complex non-linear behaviour, but just how atmospherically representative are these? For example, do they present an 'extreme' reference point with regards to bulk/surface partitioning? The simple parameterisation appears to work for 'strong' surfactants in systems with these common ions but less so for 'weak' surfactants.

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The studied aerosol compositions with surfactant anions and sodium (Na) cations are representative model systems of realistic atmospheric aerosol, specifically from marine regions, as mentioned in points (C) and (F) above. Indeed, surface tensions and surface partitioning effects in corresponding aqueous bulk mixtures have been seen to yield non-linear responses to solution concentration and solute composition changes. It must be noted, however, that in the context of atmospheric aerosol mixtures, the distinction between Na ions deriving from dissolved organic surfactant and inorganic salt does not really apply. The molecular origin of the ions present in the aqueous droplet bulk phase is irrelevant for the droplet CCN activity. In the absence of further phase changes in the droplet, other than water vapor condensation during droplet growth, only the concentration of the droplet, not the total solute mixing state, changes in considerations involving a single CCN activation cycle. It is furthermore important to distinguish between the non-linear effects of droplet composition on surface partitioning and surface tension, and of the different dry aerosol properties on the resulting CCN activity. Even with well-described aqueous solution surface tension and surface partitioning properties (isotherms), the overall effect of these properties on aerosol CCN potential is highly non-linear in response to variations in surfactant strength, surfactant solute mass fraction, and aerosol dry size (Prisle et al., ACP, 2010). As such, we cannot say that the particular systems studied, despite being composed of relatively strong surfactants mixed with a salt comprising a common cation, represent extreme cases in terms of the magnitude of surfactant effects on CCN activity (it does represent one extreme end of the isotherm). For the present aerosol compositions, the proposed simple representation works better for the stronger surfactants, but this may not necessarily always be the case and needs to be investigated further, from both an experimental and a thermodynamic description perspective.

3   Response to G. Kulkarni:

(H) The mathematical analysis shown here is really interesting. Just wondering have you compared the results or analysis with any previous measurements. On many occasions we do not had hygroscopicity (which is measured using CCN chamber) but RH and composition measurements, and the mathematical modeling described here would be really useful to fill this gap.

Unfortunately, simultaneous measurements of mixed organic-inorganic particle composition and CCN activity/hygroscopicity available in the literature are scarce. The current basis for testing the presented simple representation is therefore limited, but expanding such experimental basis is the focus of ongoing work. The aim of the representation is exactly as stated by G. Kulkarni, to provide a functional relation between composition-RH and activated aerosol fraction, which is computationally feasible and does not require detailed knowledge of composition-dependent molecular properties. It must however be noted that the presented simple representation specifically aims at describing surface active organic aerosol CCN activity, thus pertaining to activating cloud droplets, and has not been tested against measurements or thermodynamic predictions in the subsaturated (RH<100%) regime. Activating cloud droplets are much more dilute solutions than most aqueous aerosol during subsaturated hygroscopic growth. Such concentrated aqueous mixtures may actually have significantly reduced surface tensions, compared to pure water, just as the surface partitioning of surfactants may be only partial, and the simple representation presented here will therefore not apply throughout the entire droplet growth curve.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 23601, 2010.