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Interactive comment on "Connecting the solubility and CCN activation of complex organic aerosols: a theoretical study using the Solubility Basis Set (SBS)" *by* I. Riipinen et al.

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We thank the reviewer for the constructive comments which we think will be useful for improving the manuscript. Our point-by-point responses to the Reviewer's comments are below. The comments of the Reviewer are in italics and our responses in normal font.

(1) The idea of the solubility basis set is novel and promising. It excites interest in the possibility to develop accurate computationally efficient parameterizations of the evolution of solubility for large scale models. The study at hand presents only limited calculations that probe parts of the parameter space.

The proposed treatment of the organic aerosol solubility distribution does simplify the multiphase thermodynamics. However, we have covered most of the atmospherically relevant parameter space related to the coupling of organic mixture solubility and CCN activation, namely:

1) the characteristics of atmospherically relevant solubility distributions (number of compounds, solubility range, shape of distribution and assumption about organic phase activity); 2) the sizes of the particles that can act as CCN; 3) atmospheric supersaturations.

While it is true that we did not cover the range of other thermodynamic properties (e.g., densities, molar masses and surface tensions) of the organics, it was a conscious choice to isolate the solubility-related effects, which we chose to be the scope of this study – in addition to the introduction of the solubility distribution framework. Including the variation of all the other relevant thermodynamic properties of the organic compounds would be an interesting topic for future study. Furthermore, as also pointed out by Reviewer 1, to fully assess the impact of solubility on cloud formation, the results presented here need to be coupled to a model accounting for gas-particle and surface-bulk partitioning of the organics as well as atmospheric dynamics and the condensation kinetics of water vapor – framing out another direction for future work. We have clarified the justification for the chosen scope and added discussion about the potential future directions along these lines in the revised manuscript.

(2) Although the proposed treatment seems to capture the important physics, there are errors in the theory that require correction.

The major issue was related to the use of the solution density in the Kelvin term (see below). We have now repeated the calculations according to the suggestions of the reviewer and found that its impact on the presented results is small and does not affect the conclusions of the study. The manuscript has been revised accordingly.

(3) The presented main finding that is advertised - knowledge of solubility in the range of 0.1 and 100 g L-1 is most critical for modeling CCN - is already well known from past studies (e.g. Hori et al., 2003, J. Aerosol Sci.) and insufficient to merit publication of a new paper on the subject.

The Hori et al. (2003) study and a number of similar previous studies have focused on a small number of specific compounds – thus investigating only specific points in the parameter space. To our knowledge, previous studies have not systematically explored such a comprehensive set of possible solubility distributions and atmospheric conditions, including the consequences of mixture effects on solubility. This is of course something that is only achievable through theoretically generated mixtures like ours, but is also among the main strengths of our approach. Additional important contributions of our work include:

1) The introduction of the solubility distribution as a framework for representing complex organic aerosol solubility.

2) The finding that material with effective solubility above 0.1-100 g L^{-1} behaved as completely soluble for most of the approximately 6000 unique combinations of solubility distributions (representing 144 unique mixtures), particle sizes and supersaturations studied. The most important piece of information to know in this regard is the thermodynamics of the insoluble organic phase.

3) For the large range of organic mixture solubilities, particle dry diameters and supersaturations explored, the single-parameter approaches (using single ϵ or κ value to describe the solubility of the mixture) were generally sufficient to predict the activation diameters of the mixture aerosols within 10%.

4) Our results also contribute to unraveling the reasons behind the "apparent simplicity" of atmospherically-relevant complex organic mixtures (e.g. Engelhart et al., 2011). Based on our results it is clear that even with vastly different solubility distributions one can yield very similar CCN-activation behavior (and consequently values of κ or ϵ), as the parameter that matters is the material above c_t. This result is perhaps not surprising but it has not been systematically probed for such a large number of unique mixtures.

We have modified the abstract and conclusions of the revised manuscript to better highlight these findings and their novelty in relation to previous work, adding also reference to the work by Hori et al., 2003.

(4) The evaluation of the full model against the ideal mixture, kappa-model and epsilon-model seem not very relevant to me, partially attacking and deconstructing a strawman.

We respectfully disagree, although we understand that we are essentially comparing what is supposed to be a simplification of the more complex theory to the original (more complex) description. First of all, we quantitatively assess how large error in the activation diameter one makes in assuming these simplified solubility descriptions instead of the "full" picture, putting the importance of solubility into the context of the other uncertainties related to cloud-formation process. The results convincingly show that in many cases, only one parameter (either κ or ϵ) is definitely enough to accurately calculate the activation diameter in e.g. climate models. The error introduced by this simplification is negligible compared to other uncertainties. Second, while the results make physical sense, we do not think that they can be deduced without a systematic study like ours. For instance, the importance of the assumption on the organic phase interactions – which turns out to be quite important in defining c_t (and thus highly relevant for linking e.g. experimentally determined ϵ or κ to real mixture properties) at given conditions – is something that has not been clearly pointed out before.

(5) Instead, the most pressing question, how to effectively model the 50% point of partitioning (ct) in relationship to the aqueous phase formed by a mix of species with different hygroscopicties (including inorganic compounds and the dependence of the number of components) is not at all or insufficiently explored. Not varying the molecular weight and not including inorganic compounds seems to miss the most important

question: how does the aqueous phase (number of substances and their hygroscopicity) influence ct for a given solubility basis set? If inorganic or higher hygroscopic organics are present in the mix, ct should shift to lower values. In my opinion, quantifying shifts in ct in the context of the SBS and hygroscopicity of the aqueous phase ought to be the main focus of this work.

Indeed, as also indicated by the distributions present in Fig. 9 in the present paper, the c_t depends also on the number of components, supersaturation, particle size and importantly what is assumed about the organic phase thermodynamics. We have added a brief discussion of these points to the revised manuscript as well as a new figure illustrating the dependence of ct on the number of components present in the mixture as well as the molar masses of these species. These new results show that what by far matters the most is the assumption about the organic phase activity. In the case of the unity activity assumption, the dependence on the number of components is in practice the same behavior as observed in the distributions presented in Fig. 8 of the original manuscript.

While it would be interesting to do a specific study on the impact of inorganic compounds on c_t, we feel that it is out of the scope of this paper, whose target is to lay out the general framework and behavior of a large number of different solubility distributions rather than look at any specific mixtures. To the extent that we think it fits the scope of this work, we believe that the solubility distributions that have been probed also represent well the case where an inorganic component would be present – particularly as combined with demonstrating the sensitivity of the results to the molar mass. Furthermore, we have added discussion on the dependence on the c_t on molar mass and O:C ratio through including an example of atmospherically relevant organic aerosol mixture accompanied by a new figure.

(6) I suggest to include a discussion paragraph on the vision how the solubility basis may be useful beyond the immediate sensitivities that are being explored in this manuscript. It may be useful to explore this in the context of experimental data showing that the OA hygroscopicity increases are driven by evolving solubility with chemical aging as discussed in Kuwata et al., 2012, ACP and Suda et al., 2014 EST. This discussion should include computational considerations. For example, what is the current (or expected gain) from running a 10, 100, 1000 component solubility model vs a model that has could predict ct, and kappa for the aqueous phase. I performed a quick test running a solubility model with unique solubility, molecular weight, and mixing fraction and CPU time only increased when reaching 10000 unique components. Presumably the purpose the SBS to be (much) more computationally efficient and should comment and factors influencing computational speed.

This is a good idea and we have added the corresponding brief discussion about the future use of the proposed framework to the revised manuscript. We also believe that the solubility distribution can be a useful approach for modeling how the mixture hygrosopicity evolves with atmospheric age, linking it to the chemical properties of the molecules present in the mixture. In this regard, we have added references to the work by Kuwata et al. (2012) and Suda et al. (2014). Furthermore, as also stated above, we believe that the solubility distribution framework can yield useful insights in the interpretation of laboratory data for complex organic mixtures – in particular on the apparent simplicity of their CCN activation despite the well-known molecular complexity of the mixtures. Futhermore, the solubility distribution approach will probably be useful in studies investigating the relative importance of solubility versus semi-volatile partitioning (e.g. Topping et al., 2012) and adsorption effects (e.g. Kumar et al., 2009) for water uptake and CCN activation.

We have also added a brief discussion on the computational cost to the revised manuscript. Indeed, 10000 compounds is the limit where significant increase in the required computational time is expected for the simple Köhler-theory -based CCN-activation calculation. However, for large-scale models, every additional simulated species (in this case solubility bin) can increase the computational cost significantly due to the need of simulating its atmospheric chemistry, transport, removal, etc. The resolution needed for accurate treatment will require better understanding of the actual solubility distributions and their linkages with other parameters (e.g., volatility, O:C, etc.).

(7) Although there is nothing really wrong with it per se, the adoption of mass units deviates from what has been done in the past and seems awkward to me. It doesn't make the theory novel and may lead to unnecessary confusion when comparing against other manuscripts. The new part is the solubility basis set on which the focus should lie.

We assume that the Reviewer is referring to the use of mass units in expressing the solubilities – as for the mixture composition we have chosen a case where the mass and the molar units are in fact equivalent. To our knowledge expressing pure-component solubilities in g L^{-1} (or in mass per mass of water) is standard in e.g. chemical engineering handbooks, so it is difficult to know what (and which past work) the Reviewer is referring to. We would therefore prefer to keep the current units and also add some text clearly acknowledging the difference between molar and mass-based units.

(8) Eq. (1): The use of solution density in the Kelvin equation is incorrect. See Kreidenweis et al. (2005, ACP, pg. 1359). Discussion regarding the use of solution density should be removed.

This is true as we are assuming an ideal aqueous phase. We have now corrected this in all the calculations and revised the manuscript accordingly.

(9) Surface tension (Table 3, Eq. 1, pg. 28536): "calculating the surface tension as weight averages of the water and pure organic values". I am unaware for the basis for that treatment. The surface tension of the aqueous solution usually follows a logarithmic law (e.g. the Szyszkovski equation) derived from Gibbs adsorption isotherms. Furthermore, application of surface tension values derived from bulk solutions produces incorrect results since the surfactant cannot lower the free energy of the surface and contribute to the water activity simultaneously. A correct theoretical treatment will have to include accurate partitioning between the phases (Sorjamaa et al., ACP, 2004).

Since surfactant treatment is not at the center of this work, I recommend removing it completely and assuming the surface tension of pure water.

This is a valid concern. The linear weighing for mixture surface tensions is typically applicable only for hydrocarbon mixtures or other mixtures with relatively similar components (see e.g. Poling et al., 2001), and indeed more sophisticated approaches for aqueous solutions are based on correction terms applied to the surface tension of pure water (see for example Werner et al. 2014 and references therein). We have chosen the linear weighing in an effort to introduce a simple approach for the lowering effect of the organics on the water surface tension – particularly taking into account the fact that we used only one representative value for the organic surface tension. On another note, the linear approach turns out to be a reasonable approximation for succinic acid, although it underestimates the impact of the acid on the mixture surface tension (see Werner et al. 2014 and references therein). However, to avoid this kind of complexity, we have redone all the calculations assuming the surface tension of water and have updated the figures in the revised manuscript accordingly.

(10) Eq. (5): the units are a mix between mass and molar (csat is g/g and Yi is mole fraction? Maybe it is just a typo in the text below?).

Equation 5 is correct, since analogously to the gas-liquid equilibrium the organic-aqueous phase equilibrium is dependent on the mole fraction in the insoluble organic phase, as long as the activity coefficient is also expressed on a molar basis. In principle, similar formulation could be made with mass-based definitions. In our case, however, the two approaches are equivalent due to the assumption of constant molar mass throughout the organic mixture. We have clarified this in the revised manuscript.

(11) The statement that "water -solubility determines the aerosol water content at equilibrium" is wrong or only partially correct, depending on how one views the problem. The water content at equilibrium is controlled by RH, surface tension, and the molecular weight and activity of the dissolved components. If all components are dissolved,

solubility exerts zero control on aerosol water content (as acknowledged in the paper).

True. We have rephrased this sentence in the revised manuscript.

(12) The distinction between ideal mixture vs unit activity model is unclear. In an ideal solution, the activity coefficient of each component is equal to unity. Thus, the two models are semantically identical. Despite several attempts I am unable to extract from the paper how the two cases are different.

In the ideal mixture the activity coefficient is unity, meaning that the effective solubility of a given component i scales with the composition of the insoluble organic as indicated by Eqs. 1 and 2. In the unity activity case, on the other hand, the mixture activity (the product of activity coefficient and mole fraction) is unity – indicating that the individual components dissolve to water in the same way as they would if they were present in their pure form. We have added this clarification to the revised manuscript.

(13) Comparing the limited solubility model to the full dissolution model is a straw man argument. Of course they will agree if all species will dissolve, disagree if they do not, and the disagreement will be proportional to ct. It is trivial that if one breaks the assumption of a model that it won't work. I suggest removing that discussion from the paper.

We understand the point that the Reviewer is making, but think there is indeed value in quantifying the actual differences in activity diameter predictions – given that we have explored a large fraction of all atmospherically relevant cases. This helps in putting the importance of solubility in context with other potential uncertainties present in modeling the atmospheric cloud formation processes. What we also think is remarkable in our results is that assuming a single c_t for all the mixtures yields a reasonably good prediction of the soluble fraction and thus the activation diameters.

(14) As far as I can tell, the epsilon model and the kappa model are identical since kappa = epsilon kappa_max and kappa_max is fixed in the study. Therefore figures*

7a,b are redundant, as are figures 11, c,e. There may be merit to keeping both treatments if molecular weight of the organic is allowed to vary.

This is partly true, as κ and ϵ are directly related. However, the sensitivity of the activation diameter to these parameters is different, since when the ϵ model is used, more information needs to be given in the fitting process. However, the results shown in Fig. 6 of the discussion paper show that this information does not make a big difference in the predicted activity diameters – although there is a small effect seen in the narrower quartile range present for the ϵ model.

(15) Figure 7b suggests that there are numerical issues with the model. How can the fitted kappa exceed kappa max?

This was due to using the solution density and surface tension in the Kelvin term of the full model calculations while this information was not given to the simplified schemes. As suggested by the reviewer, we have now repeated all the calculations assuming the surface tension and density of pure water, and have modified the related figures accordingly.

(16) It would be helpful to include isolines of epsilon in Figure 3,b to visualize the range of solubilities probed by the model.

This is a good suggestion and we have redrawn the corresponding figure adding the suggested isolines.

(17) Page 28534, line 5 to end of paragraph: Is it necessary to list how many Köhler curves were made? More interesting would be e.g. calculations of d(property)/d(other property) in your calculations.

Indeed, the total number of the Köhler curves is perhaps not that interesting, but reason we have included the number of the activation points just to illustrate the number of different combinations of solubility distributions, particle sizes and supersaturations we investigated. We are not sure what the reviewer means by calculations of d(property)/d(other property), and would prefer to keep the description as it is.

(18) Page 28525, Typo line 11, "Aalbrecht"

We have corrected the typo.

(19) Page 28525, Line 19-25: connect with "and' ?

We have corrected the typo.

(20) Page 28526, Line 5, "than pure compounds"

We have modified the revised manuscript accordingly.

(21) Page 28526, Line 27, kappa does not strictly vary between 0 and 1, I think this is misleading as it suggests that kappa is a ratio.

We have clarified this in the revised manuscript.

(22) Page 28526, Paragraph beginning on line 20: I think this paragraph oversimplifies the different representations of solubility in CCN activation studies. Furthermore Table 1 does not aid in the understanding of the paragraph or the simplifying assumptions. I would recommend removing Table 1 and expanding the paragraph.

We have expanded the paragraph as suggested. However, without further information it is difficult to know what oversimplification the Reviewer refers to, and would prefer to keep the table as it is.

(23) Section 2.1.1: The section heading does not reflect the content.

We have revised the title to read "Equilibrium between water vapour and an aqueous phase containing dissolved material"

(24) Page 28540, Line 17, change "practise" to "practice"

Corrected.

(25) Pg 28543, Line 4: "correlaction" to "correlation"

Corrected.

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