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.

Anonymous Referee #2

Received and published: 30 January 2015

Riipinen et al. present a theoretical study of CCN activation. The manuscript introduces the concept of a solubility basis set to model a particles composed of a mixture organic compounds where each compound has a unique solubility. The main findings of the study are that accurate knowledge of solubility in the range of 0.1 and 100 g L-1 is most critical for modeling CCN activity, while accurate representations of solubility outside that range are less critical. The study also tests the ability of single parameter representations to capture the CCN activation behavior of the mixture.

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. Whilst it is in principle suitable for ACP, the study is under-developed and will require significant improvement before it can be published. Although the proposed treatment seems to capture the important physics, there are errors in the theory that require correction. 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 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 straw man. 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. It is my recommendation that they authors fix the theoretical issues and present a revised, refocused, and strengthened manuscript for further review.

Specific comments

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.

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 ES&T.

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.

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. I have several concerns regarding the theoretical framework:

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.

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.

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

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).

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.

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.

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.

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

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

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.

Other comments:

Page 28525, Typo line 11, "Aalbrecht"

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

Page 28526, Line 5, "than pure compounds"

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.

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.

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

Page 28540, Line 17, change "practise" to "practice"

Pg 28543, Line 4: "correlaction" to "correlation"

––––––––––––––––––––––––––––––

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 28523, 2014.