Review of
Cloud droplet activation of secondary organic aerosol is mainly controlled by molecular weight, not water solubility

Wang, Shilling, Liu et al. showcase a series of experiments measuring organic aerosol hygroscopicity expressed as $\kappa_{\mathrm{CCN,\,org}}$ using a condensation particle counter and a CCN counter. Their chamber experiments span common SOA precursors with varying inorganic (ammonium sulphate) to organic volume ratios. To explain the experimental results, the authors use previously published relationships for volatility to molecular weight and $\kappa_{\mathrm{CCN,\,org}}$ to molecular weight. They presented an analysis of the major factors affecting the hygroscopicity parameter of the organic aerosol formed, assuming complete dissolution at high relative humidity (RH). The molecular weight of the organic compounds is highlighted as a major factor in determining the apparent hygroscopicity parameter at high RH.

This work is well within the scope of Atmospheric Chemistry and Physics, and is of general interest to the community and discusses new findings. The paper is based on solid experimental work which is largely described in the Supplementary Information, some of which is suggested to be moved into the main manuscript. However, in this referee's opinion, the presentation of the findings and the logic of the explanations reveal a lack of clarity and certain flaws in the argumentation that should (and can) be addressed. Therefore, the manuscript requires major revisions and additional supporting evidence for the assumptions made. More clarity is especially needed for the definition and use of the terms 'water solubility' and 'hygroscopicity' as pointed out below. The organic hygroscopicity addressed in this paper specifically targets the high relative humidity or supersaturated regime. There needs to be an increased specificity on where, at approximately infinite dilution, the presented modeling results and the provided interpretation apply. The paper also needs more specificity in the use and validity of Eq. (2). General and specific comments are detailed in the following.

General comments

1. Clarity on Hygroscopicity Needed:

Hygroscopicity is a nebulous term which needs to be defined. Hygroscopicity can be defined as the mass of water per mass of solute at a given RH or water activity or the equivalent ratios using moles or volumes – or in a different way. Hygroscopicity is not equal to $\kappa_{\mathrm{CCN,\,org}}$, but the authors implicitly assume just that (page 3 line 19) and elsewhere in the manuscript. Introducing and defining κ as a hygroscopicity parameter should be added to the introduction. Moreover, κ is not a material constant, since in reality, it may depend on the relative humidity range. For example, changes in κ as a function of RH for different SOA have been shown, among others, by Rastak et al. (2017).

The authors need to specify that their measurements are κ at CCN activation (i.e., $\kappa_{CCN, org}$) and do not directly translate to subsaturated hygroscopic growth factors ($\kappa_{HGF, org}$). Therefore, the papers title and main conclusion do not apply to subsaturated RH conditions. From the context of the measurements, I can infer that the discussion is on $\kappa_{CCN, org}$, but the reader should not have to do that.

2. Clarity on Solubility Needed:

Water-solubility is not currently defined in the introduction. It can either be the solute saturation point (limit of solubility) of a solid-liquid equilibrium or it could refer to the transition from liquid-liquid equilibrium (miscibility limitation as mentioned in the supplementary information) to a single aqueous phase. The solubility values of those variants likely differ and, according to equilibrium thermodynamics, depend on the other species in an aqueous solution. Providing a quantitative definition earlier in the paper (currently one needs to read until page 9 to find one), would also help distinguishing the differences between water-solubility (C), and apparent $\kappa_{CCN, org}$. The introduction would benefit from having the general definition of hygroscopicity early on. This change will make it clear to the reader that organic hygroscopicity may change over the full water activity range, complete dissolution occurs at some RH value, depending on the other mixture species, and $\kappa_{CCN, org}$ is at water supersaturation RH.

On a related point, in the SI (section 6, page 12, line 20) the authors assumed miscibility transition of 0.5 O:C, does this include a salting-out effect or does it assume only water-organics phase separation? In this discussion on miscibility, the observational work performed by Renbaum-Wolff et al. (2016) on SOA liquid–liquid phase separation at high relative humidities should be included.

Could the authors add some discussion on how the interpretation would change (or not) if the particles were phase-separated (water and organic-rich phases) during the CCN measurement? Especially, given the context of recently published work by Ovadnevaite et al. (2017) on phase-separated CCN activation.

3. Community claims need support and clarification:

The statement on page 4 line 9-12 needs a justification, as well as a similar statement in the abstract (page 2 line 13-15): “Earlier studies showed organic hygroscopicity increases nearly linearly with oxidation level. Such increase of hygroscopicity is conventionally attributed to higher water solubility for more oxidized organics.". Claiming that an increase in polarity leads to an increased solubility and then higher $\kappa_{\mathrm{CCN,\,org}}$ is a "long held hypothesis" needs to be corroborated by citation of relevant references. At least this referee does not share the opinion that the higher water-solubility was the main hypothesis in "the community". Jimenez et al. (2015) showed a relation between O:C and $\kappa_{\mathrm{CCN,\,org}}$, whereas Riipinen et al. (2015) showed a relation between solubility and $\kappa_{\mathrm{CCN,\,org}}$. There is no citation provided linking O:C and solubility. On page 4 line 14-16, the citation Kuwata et al. (2013) does show a loose trend of O:C with $\kappa_{\mathrm{CCN,\,org}}$, but the author's statement neglects the fact that molar mass as well as density are changing with O:C. In the same sentence, the Petters et al. (2009) citation is confusing; as Petters et al. (2009) does not discuss the oxidation level, but discusses molar volume. If the authors are reinterpreting the results of Petters et al., (2009) and Petters et al., (2016) through an O:C lens and neglecting the covarying molar mass that should be stated.

An increase in organic polarity could increase water affinity, but to change solubility, the molecular size and, for solid-liquid solubility, the crystal structure, is also playing an important role (e.g. consider the well-known odd-even alteration with carbon atom number in the water-solubilities of dicarboxylic acids; e.g. Bilde et al., 2003). Changes to solubility would depend on the combination of molecular size, molecular interactions in solution, which would include polarity, and crystal structure (unless liquid-liquid miscibility is meant).

4. More Support for Eq. 2:

The applicability and usability range of Eq. 2 needs to be discussed. This discussion is even more warranted since Sullivan et al. (2009) used Eq. 2 for mineral dust, not organic molecules.

Starting with the definition of κ from Petters and Kreidenweis (2007) (their Eq. 2), one can derive Eq. 2 shown in this manuscript as a limiting case. Note, one must substitute water activity for the water mole fraction and activity coefficient. In doing this, one can show the assumption of $i = 1$ is valid only under conditions of high dilution in water, when the activity coefficient and the mole fraction of water each approach one. Due to the activity coefficient being depended on the organic's O:C and molecular structure, it is likewise true that i is also dependent on those same properties in non-dilute cases. Such a derivation and pertinent discussion would make the origin and limited range of application of Eq. (2) clear. This is important since much of the argumentation about the role of molecular weight (i.e. molar mass) is built based on assuming Eq. (2) to be valid or at least to be a valid approximation.

The authors should add more to the discussion of the previous uses of Eq. 2. In the paper's current state, the reader could have the impression that the control of $\kappa_{\mathrm{CCN,}}$

$_{org}$ by M_{org} is a brand new discovery. That impression would be incorrect when we consider the following quotation:

> *"For highly soluble particles,* ***CCN activity is dominantly controlled by molar volume, which is determined by both ρ_{org} and $1/M_{org}$*** *(Eq. 5) (Petters et al., 2009a). Kuwata et al. (2012) developed a method to predict ρorg using O : C and H : C ratios. According to the method, ρ_{org} is higher for highly oxygenated compounds. Even so, the range in ρ_{org} values for O : C>0.6 from 1100 to 1650 kgm^{-3} is not sufficient to explain the variability observed for κ for highly soluble materials. Furthermore, the* ***ρ_{org} values of carbohydrates and synthetic polymers do not vary significantly*** *yet the variations in κ is significant (cf. Supplement).* ***The implication is that the dominant regulator of CCN activity is M_{org}*** *for highly soluble particles."*
>
> *-Kuwata et al., 2013*

The authors' experimental work does extend the above result by Kuwata et al. (2013) to SOA systems. But, the authors did not place their results within the context of the previously published work, which similarly uses Eq. 2 with organic compounds. Also, it is clear that assuming density of organics to remain constant upon oxidation is only an approximation, since with increases in O:C and molar mass, density may also vary by up to ~ 40 %.

5. Discussion in the Supplemental Information:

There are a couple of topics that were fully discussed in the Supplemental Information that would better serve the reader in the main text. I suggest moving some of SI part 6 on liquid-liquid phase separation into the main text either in the introduction or section 3.3 – 3.4. In addition, the authors could add some of the Monte Carlo error assessment to the main text as well.

The simulations of the solubility distributions in the SI are quite informative. I suggest bringing some of that information into the main text or into Figure 2.

Specific comments

1) Page 2 Lines 7, 12, 18, 19: Is it hygroscopicity or is it hygroscopicity parameter?

2) Page 2 Line 12: Add the following…*not limited by solubility* at CCN activation RH, *but …*

3) Page 3 Line 19: Change hygroscopicities to hygroscopicity parameters.

4) Page 4 Line 7: Change hygroscopicity to hygroscopicity parameter.

5) Page 5 Line 1: Change atmospheric to atmospherically.

6) Page 5 Line 3: Add the following…*organic hygroscopicity* at CCN activation RH *is not limited.*

7) Page 5 Line 5: This statement "*hypothesized earlier*" needs a citation.

8) Page 5 line 4-6 as well as Page 21 line 16-20: These statements led to some confusion as to whether the authors are referring to the size of the precursor molecule or the oxidation products. In the same vein does the title refer to the precursor or the oxidation products?

9) Page 6 Line 16: Add specificity…*are the* dry or water free *volume fractions…*

10) Page 6 Line 17: Add the following…*hygroscopicity*~~*ies*~~ parameters *of the organic*~~*s*~~ mixtures *and…*

11) Page 7 Line 1: Add specificity to x_{as}, is this dry or wet mixture and under what RH.

12) Page 7 Line 2: What is the chamber RH?

13) Page 7 Line 3: Add the surface tension that was assumed when deriving $\kappa_{\mathrm{CCN,\,org}}$.

14) Page 11 Line 19: Add…*miscibility limitation* at supersaturated RH.

15) Page 13 Line 20: "*same behavior as pure components*" That statement is incorrect due to mutual solubility, see Marcolli et al., (2004). The same applies to the statement on line 21 – 22; it is not the mass that matters, but the mixing.

16) Page 14 line 2: The solubility values of the pure components may not apply, but potential miscibility limitations due to liquid-liquid phase separation still applies to amorphous physical states. Please discuss. Also, by "amorphous organic state" likely "amorphous physical state" or phase state is meant.

17) Page 14 line 6 and line 8: Add comma after *…particle,* and after *Fig. 2,*

18) Page 14, line 22: A narrow density is true, but molar volume (M_{org}/ρ_{org}) is used in Eq. 2, and molar volume does vary. A statement on the relative impact that M_{org} and ρ_{org} have on molar volume would provide a stronger justification here.

19) Page 17 line 8: "*non-ideal solution effects are negligible*" Are they negligible? A justification is needed.

20) Page 18 line 3: Add…*due to* Eq. 2, *their lower…*

21) Page 18 line 6: Change hygroscopicity to hygroscopicity parameter.

22) Page 18 Eq 3: Use $\log_{10}$

23) Page 18 line 12: Jargon used; specify that this is the number of atoms.

24) Page 19 Line 11: Add…*leading to a lower hygroscopicity* parameter via Eq. 2.

25) Page 19 line 13: Change volatility to volatilities.

26) Page 19 line 14: Use $\log_{10}$

27) Page 19 line 21 & 20: Change hygroscopicity to hygroscopicity parameter.

28) Page 19 line 21: Add…*during* the *recent…*

29) Page 20 line 5: Add "at CCN activation, i.e. supersaturated conditions."

30) Page 21 line 5: Change oxidize to oxidized

31) Page 21 line 11: Change hygroscopicity to hygroscopicity parameter

32) Page 21 line 13: Add… at CCN activation *is controlled by…*

33) Page 21 line 14: "*mainly by the molecular weight of the organic species*" This is the case for SOA due to the gas–particle partitioning affecting O:C and molar mass simultaneously. That concept should be added.

34) Page 25 caption: *…50 nm* dry diameter *ammonium…*

…*hygroscopicity* parameter at high RH? *is shown as a function of* dry particle *sulfate*…

35) Figure 4 needs clarification in the x-axis label or caption that it is the carbon number of the SOA products.

36) The paper's title alongside Figure 5 is confusing and needs clarification. Given the title of the paper, why is the exact opposite shown in Figure 5, i.e., increasing O:C with increasing $\kappa_{\mathrm{CCN,\,org}}$. Why not plot molecular weight vs. $\kappa_{\mathrm{CCN,\,org}}$? Then the spread in the data would be the O:C dependence, which would reflect the main point of the paper.

References

Bilde, M., Svenningsson, B., Mønster, J. and Rosenørn, T.: Even-odd alternation of evaporation rates and vapor pressures of C3-C9 dicarboxylic acid aerosols, Environ. Sci. Technol., doi:10.1021/es0201810, 2003.

Kuwata, M., Shao, W., Lebouteiller, R. and Martin, S. T.: Classifying organic materials by oxygen-to-carbon elemental ratio to predict the activation regime of Cloud Condensation Nuclei (CCN), Atmos. Chem. Phys., 13(10), 5309–5324, doi:10.5194/acp-13-5309-2013, 2013.

Marcolli, C., Luo, B. and Peter, T.: Mixing of the Organic Aerosol Fractions: Liquids as the Thermodynamically Stable Phases, J. Phys. Chem. A, doi:10.1021/jp036080l, 2004.

Ovadnevaite, J., Zuend, A., Laaksonen, A., Sanchez, K. J., Roberts, G., Ceburnis, D., Decesari, S., Rinaldi, M., Hodas, N., Facchini, M. C., Seinfeld, J. H. and O' Dowd, C.: Surface tension prevails over solute effect in organic-influenced cloud droplet activation, Nature, 546(7660), 637–641, doi:10.1038/nature22806, 2017.

Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity – Part 2: Including solubility, Atmos. Chem. Phys., 7(8), 1961–1971, doi:10.5194/acp-7-1961-2007, 2007.

Petters, M. D., Kreidenweis, S. M., Prenni, A. J., Sullivan, R. C., Carrico, C. M., Koehler, K. A. and Ziemann, P. J.: Role of molecular size in cloud droplet activation, Geophys. Res. Lett., 36(22), 1–5, doi:10.1029/2009GL040131, 2009.

Petters, M. D., Kreidenweis, S. M. and Ziemann, P. J.: Prediction of cloud condensation nuclei activity for organic compounds using functional group contribution methods, Geosci. Model Dev., 9(1), 111–124, doi:10.5194/gmd-9-111-2016, 2016.

Rastak, N., Pajunoja, A., Acosta Navarro, J. C., Ma, J., Song, M., Partridge, D. G., Kirkevåg, A., Leong, Y., Hu, W. W., Taylor, N. F., Lambe, A., Cerully, K., Bougiatioti, A., Liu, P., Krejci, R., Petäjä, T., Percival, C., Davidovits, P., Worsnop, D. R., Ekman, A. M. L., Nenes, A., Martin, S., Jimenez, J. L., Collins, D. R., Topping, D. O., Bertram, A. K., Zuend, A., Virtanen, A. and Riipinen, I.: Microphysical explanation of the RH-dependent water affinity of biogenic organic aerosol and its importance for climate, Geophys. Res. Lett., 44(10), 5167–5177, doi:10.1002/2017GL073056, 2017.

Renbaum-Wolff, L., Song, M., Marcolli, C., Zhang, Y., Liu, P. F., Grayson, J. W., Geiger, F. M., Martin, S. T. and Bertram, A. K.: Observations and implications of liquid–liquid phase separation at high relative humidities in secondary organic material produced by α-pinene ozonolysis without inorganic salts, Atmos. Chem. Phys., 16(12), 7969–7979, doi:10.5194/acp-16-7969-2016, 2016.

Riipinen, I., Rastak, N. and Pandis, S. N.: Connecting the solubility and CCN activation of complex organic aerosols: A theoretical study using solubility distributions, Atmos. Chem. Phys., 15(11), 6305–6322, doi:10.5194/acp-15-6305-2015, 2015.

Sullivan, R. C., Moore, M. J. K., Petters, M. D., Kreidenweis, S. M., Roberts, G. C. and Prather, K. A.: Effect of chemical mixing state on the hygroscopicity and cloud nucleation properties of calcium mineral dust particles, Atmos. Chem. Phys., 9(10), 3303–3316, doi:10.5194/acp-9-3303-2009, 2009.