

Interactive comment on “Cloud condensation nuclei activity, droplet growth kinetics and hygroscopicity of biogenic and anthropogenic Secondary Organic Aerosol (SOA)” by D. F. Zhao et al.

Anonymous Referee #1

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The manuscript “Cloud condensation nuclei activity, droplet growth kinetics and hygroscopicity of biogenic and anthropogenic Secondary Organic Aerosol (SOA)” by D.F. Zhao and co-authors deals with sub- and supersaturated hygroscopicity of chamber generated SOA from representative anthropogenic and biogenic precursors, relating observed differences to chemical variations in terms of oxidation state and mixing between each SOA component. The paper is interesting in relation to both aerosol thermodynamics, atmospheric chemistry and aerosol modelling accounting for effects of chemical ageing. It is well-written and the discussion is overall good. I do however

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have some additional suggestions for clarifications and to elaborate a bit further.

General comments:

Although I generally think the discussion is very good, the manuscript would benefit if some of the clarity in the conclusions section would be evident already at the discussion stage.

The consequences for atmospheric studies of exactly the processes (SOA mixing) and SOA types studied could be emphasized a bit further.

Concerning the description of the experiments, it could be clarified whether the ageing processes are considered to occur in both the gas and aerosol phases, or only in the gas-phase. I was somewhat unsure of this in relation to the mixed A- and BSOA studies and it certainly affects the interpretation of mixing and other thermodynamic effects vs. kinetics and the plausibility of oligomerization. What’s the basis of the different time lags chosen for mixing A and B VOCs? Do you have homogeneous nucleation in the chamber, there is no mention of seeds?

I am not sure how well oligomer formation explains the hygroscopicity and CCN activity results. Is oligomerization the most plausible explanation for the non-linear response in K to A and BSOA fractions? It could also be non-ideal solution effects, such as co-dependent solubility, possibly also leading to evaporation of some SOA material. You could either explain in more detail what makes you believe there should be oligomers in the aerosol, e.g. give a few more references to previous work supporting this, or explore other explanations, such as solubility and co-solvation effects, in a bit more detail. These would be supported by the sub-unity $K(\text{HTDMA})/K(\text{CCN})$ ratios? Instead of chemical pathways to reducing volatility, have you considered also thermodynamic explanations, such as Raoult’s law mixing (see e.g. Asa-Awuku, 2009)? Alternatively, how would you make a future experiment to get a positive detection of these oligomers?

Why would organic-organic interactions decreasing particle volatility and SOA persis-

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tence lead to increases in CCN activity? In fact, ideal mixing of organic components (organic phase) would indicate strong similarities between the different SOA types and therefore potentially an unchanged CCN activity of their mixtures, as indeed observed.

Similar droplet growth kinetics doesn't necessarily mean particles are internally well-mixed. The presence of water could lead to melting of one organic phase which could then facilitate melting of another organic aerosol phase. Maybe you could clarify a bit what significance you put on the similar growth kinetics?

How are the error bars shown on K values estimated? These K values are fairly low (<0.1), but it still seems that differences are significant and outside uncertainty limits?

Specific comments:

19913 I. 18-20: "Since different SS correspond to different critical sizes, this dependence indicates a size dependent chemical composition of aerosol (Zhao et al., 2015a)." Couldn't it also be dilution state and concentration dependent behavior in the aqueous phase. What would be the mechanism for size dependent composition?

19915 I. 13-16: "Functionalization does not significantly change the molar volume of organics, but it increases the van't Hoff factor due to both its interaction of polar functional groups with water and additional dissociation effects by carboxylic and hydroxyl group (as in Eq. A6) (Petters et al., 2009; Tritscher et al., 2011)." What do you mean by the first part of this statement? Which interactions and how do they change the van't Hoff factor? How do you define the van't Hoff factor?

19915 I. 19: Here you briefly mention the effects of oligomerization on surface tension effects. I was a bit confused until reading on and you may consider mentioning this either in relation to the other surface tension discussion or after discussion oligomers in more detail. Maybe also clarify exactly what compensating effects of surface tension you are discussing here?

19916 I.18: less significant as / less significant than?

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19917 I.17: similar with / similar to?

19918 I.1-7: The paragraph concerning mixing and the work of Hildebrandt et al. (2011): here it is not entirely clear if you are talking about an ideal organic-organic mixture or an ideal aqueous mixture with respect to each of the organics. For the latter option, I wonder what you consider the phase of the particles to be? For high viscosity or solid particles, it could of course affect the mixing state upon sequential addition to the reaction mixture. Also, I assume you are aware of that there is no reason to expect that an ideal organic mixture would entail that either organic would behave ideally in aqueous solution, but it is unclear from this paragraph, so I suggest you elaborate a bit on this very interesting issue.

19920 I. 2-3: What exactly is meant by simple linear mixing and a non-linear response, respectively? You do explain this, but I would define it rigorously before using these terms simply. What is the measured response, change in $K(\text{HTDMA})$? Is it linear with respect to amount of AVOC and BVOC, or ASOA and BSOA? Also, is it ASOA and BSOA mass or volume fraction?

19921, I. 1-6: Regarding morphology, considering the growth kinetic results, is this really a plausible explanation? If both types of SOA have similar growth kinetics to ammonium sulphate, how would morphology explain non-linear effects on mixed particle K? I understand the experiments are made in different humidity regimes, but wouldn't any differences be enhanced at CCN conditions? You may want to explain this further.

19922, I. 9: Regarding the interpretation of potential surface tension effects, if the surface tension effect of BSOA would be greater than for ASOA, in the sense that surface tension is lower at CCN activation for BSOA, this should in my opinion lead to a smaller observed discrepancy between $K(\text{HTDMA})$ and $K(\text{CCN})$ for BSOA, since at both humidity conditions there would then be a positive bias on K. Also, if surface tension effects were significant for BSOA, then I would expect subsaturated hygroscopicity of BSOA to be greater than for ASOA, opposite to what is reported. However, surface

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tension effect are complex and maybe you can clarify your line of reasoning a bit further?

1992, I. 24: Concerning evaporation and condensation causing potential artifacts, what are the respective residence times at sub- and supersaturated water uptake? Again, I don't immediately see how the limited diffusivity would be a plausible explanation for the K discrepancy when the growth kinetics are similar?

Reference:

Asa-Awuku, A. et al. Mixing and phase partitioning of primary and secondary organic aerosols, *Geophys. Res. Lett.* 36 (15), 10.1029/2009GL039301, 2009.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 15, 19903, 2015.

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