

## ***Interactive comment on “Alkene ozonolysis SOA: inferences of composition and droplet growth kinetics from Köhler theory analysis” by A. Asa-Awuku et al.***

**A. Asa-Awuku et al.**

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We would like to thank the referee for the very thorough and thoughtful comments; our responses follow.

### **General comments**

*The use of critical supersaturation vs. dry diameter measurements to infer multiple solute properties cannot be supported independently. As I explain below, it has been shown that CCN activity does not necessarily correlate with solute molecular weight. Moreover, values of some parameters must be assumed before others are inferred. These assumptions must be clearly stated so the reader understands the basis under which the remaining parameters are derived.*

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We have made sure to clearly state all assumptions made.

*1a. If classical Köhler theory would hold, i.e. equations (3) + (4) apply, then CCN activity should strongly correlate with solute molecular weight, and forward calculations should agree with measurements. This is contradicted by observations. Dinar et al. (2007) report CCN activity for fractionated HULIS samples of different molecular weight ranges, termed F1 (0.2 - 0.5 kDa), F2 (0.5 - 1.0 kDa), F3 (1 - 3 kDa), F4 (3 - 10 kDa), and F5 (10 - 30 kDa). The critical dry diameter at  $s = 0.2\%$  is nearly identical for F1, F2, F3 ( $\sim 165$  nm) and slightly smaller for the high MW compounds:  $\sim 192$  and  $212$  nm for F4, and F5, respectively. Similar discrepancies between solute molecular weight and molecular weight inferred from growth factor measurements were observed by Gysel et al. (2004), Brooks et al. (2004), and Baltensperger et al. (2005).*

These are all important points, and present issues that one needs to be aware of when applying KTA. We are analyzing the soluble fraction extracted from filters and not the parent aerosol. This excludes insoluble polymers from the analysis, and focuses on the (soluble) low molecular weight fraction of the parent aerosol, which is expected to contribute to most of its hygroscopicity. Furthermore, CCN activity is measured over a large range of supersaturations and find that  $s_c$  vs.  $d_{dry}$  is consistent with “classical” Köhler theory (hydrolysis of oligomers, if present, would likely perturb the simple behavior seen). Given this, and that our inferred molar volumes are consistent with known speciation of the aerosol, inferred molar volumes are likely representative of the samples; this suggests that KTA, if applied intelligently, can provide insight on the chemical nature of the aerosol. This is fortunate, because the framework used to describe the hygroscopicity of the aerosol (being KTA,  $\kappa$ -Köhler or  $\rho$ -ion Köhler theory) should represent reality.

The studies cited by the reviewer do suggest however that issues arise when the inferred molecular weights are much larger than the 100-200 Da inferred for the samples here; we note this in the manuscript.

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As a side note, the amount of water available in hygroscopic growth studies is drastically less than that available during CCN activation; limited solubility of the parent aerosol, shifts in the monomer/oligomer equilibria, surface tension effects and departures from non-ideality can all affect hygroscopic growth and complicate analysis for inferred properties.

*These observations suggest that Kohler theory with its basis in Raoult's law may not generally apply to atmospheric organic aerosol. Petters et al. (2006) suggest the use of Flory-Huggins theory, which describes water activity for aqueous solutions containing high molecular weight compounds. Based on their Figure 6 both CCN activity and hygroscopic growth become insensitive to molecular weight as suggested by the experimental studies. This implies that molecular weight and activity coefficients are correlated for high molecular weight compounds. This can also be seen from Mikhailov et al. (2004) who investigated BSA, a protein with molecular weight of  $\sim 66$  kDa. In their Figure 2 they show that the molal osmotic coefficient (which is approximately equal to the effective van't Hoff factor used in this study) is a strong function of solution molality and that values of the molal osmotic coefficient exceed 100 for molalities greater than 0.1 moles per kilogram of solvent. In the present study a value of unity was assumed introducing a potential error of two orders of magnitude on the observed molecular weights.*

These studies show that the solute term may lose its dependence on molar volume once the latter becomes large. This just suggests that KTA should be applied only when it corresponds to compounds with small molecular weight (such as in the samples studied here).

*1b. Another important point is that there is only limited information contained in a series of critical supersaturation vs. dry diameter measurements. As the authors state the data "are well represented with a power law consistent with a  $d^{-3/2}$  dependence". A trace of critical supersaturation ( $sc$ ) vs. dry diameter ( $d$ ) for one aerosol type is fitted to what the authors call INCA parameter This is identical to the parameterization used*

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*by Fitzgerald and Hoppel (1982) and Snider and Brenguier (2000) and also very similar to other single parameter representations of Kohler theory that have been suggested in the literature (Hudson and Da, 1996; Rissler et al., 2006; Petters and Kreidenweis, 2007; Wex et al., 2007). From this single measured quantity the authors deduce  $M_s$ ,  $-s$ , (the effective van't Hoff factor containing the activity coefficient and the numbers of ions the molecule dissociates into). Clearly the solutions are not unique; an infinite number of possible combinations of  $M_s$ ,  $-s$ , can produce the same  $!$ . Some of these properties may be guessed within a factor of two, for example solute density and dissociation state, but they can certainly not be retrieved independently, even if activity coefficients and solute molecular weight (see previous comment) are not correlated. In the framework presented in the manuscript it is also assumed that mixtures behave ideally, i.e. in Equation (9) which says that if the inorganic properties are known the organic properties can be retrieved without error.*

KTA is in our view, one more "tool" available to the scientific community for understanding the source of hygroscopicity of organic CCN. We never advocated a general application of KTA to any type of aerosol (especially in-situ measurements), nor do we ever claim it can deduce all the parameters mentioned above. However, if sufficient constraints are satisfied, average molar volume and surface tension depression can be inferred. First, auxiliary information (density, inorganic composition for the van't Hoff factors) must be available from independent measurements. Second, KTA should be applied when most of the solute comes from the organic phase, when the soluble fraction of the organic is known (e.g., when extracted from filters), and when the organic molar volume is small so that its hygroscopicity correlates with molar volume (this can be assessed after application of KTA).

Satisfying the restrictions above, we have shown (in independent studies) that useful information can be derived with KTA. For example, molar mass inferences is reproduced for CCN with mixtures of known composition (Padró et al., 2007), is consistent with known speciation of monoterpene and sesquiterpene SOA (Asa-Awuku, 2009; En-

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glehart et al., 2008) and surface tension depression of primary marine organics (Moore et al., 2008).

*The arguments justifying the inferred molecular weights and surface tensions made in Section 3 are circular. It is first argued that the particles are not surface active (pg. 8992, see also other comments later), but then on pg. 8993, a depressed surface tension of 60 mN m<sup>-1</sup> is argued for. This value is justified with the observation that the effective molecular weights inferred from this method did not otherwise agree with what was reported in Gao et al. (2004). It is never clear whether the data from Gao et al. validates KTA or if it is used to constrain the surface tension retrieval. It is then concluded that on pg. 8995 and abstract that “surfactants are likely present”, that “water soluble organics are composed of low molecular weight species with a molar mass of 200 g per mol”, and “HULIS are not an important component of the WSOC fraction”. This certainly cannot be concluded from a single measurement of !.*

The arguments are not circular, as the amount of independent information is more than the parameters constrained. The method however is iterative, and we believe this is why the impression of a circular argument was made. Moore et al. (2008) present the method in detail; King et al., 2009 have also implemented a similar approach to infer surface tension of monoterpene SOA.

We have removed the discussion on HULIS, as indeed we cannot make that deduction.

*2. It would be helpful to place the measurements presented here in the context of CCN activity for SOA from similar precursors published in the literature (Hegg et al., 2001; Saathoff et al., 2003; Huff-Hartz et al., 2005; VanReken et al., 2005; Prenni et al., 2007). For example hygroscopicity measured here appears significantly larger than obtained in situ for SOA sampled directly from a smog chamber. Some of the difference may be due to the different precursors and also experimental methods used (e.g. filter extract vs. online measurement, presence of an OH scavenger etc.). To compare hygroscopicity it would be useful to report equivalent single parameter fits.*

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*... and 298.15 K.*

This is an excellent point and we have included such calculations in the text. We would like to note however, that calculation of the “kappa” (or other parameter) is based on Köhler theory, hence subject to some of the same theoretical limitations as KTA.

*3a. The XAD-8 resin column TOC technique presented in Sullivan and Weber (2006) is only sensitive to low molecular weight compounds with less than 4-5 carbon molecules. Recovery from the hydrophobic fraction is not complete and uncertain. Since only 34% (Cycloheptane), 44% (1-methylcycloheptane), and unknown amounts (Terpinolene) of the species are low molecular weight the WSOC number in Table 2 are misleading since the entire extract was used to generate the particles. Was the sample filtered to remove insoluble particles that may have been introduced into the solution during the sonication before atomization? If not then water insoluble and higher molecular weight compounds may have contributed to the carbon mass, but would not be accounted for in TOC analysis, potentially skewing the reported AS/extract mixing ratios.*

We never used XAD-8 resin columns in this study.

The samples were ultra-filtered for the reasons presented above.

*3b. It should also be noted that the chemical analysis in Gao et al. was done using LC-MS from methanol extracts and thus the chemical speciation presented in Table 1 is not necessarily applicable to the atomized water extracts presented in this study.*

We have noted this potential artifact. Nevertheless, the compounds extracted are hydrophilic and are expected to be present in the atomized solutions.

*4. It would be helpful if the authors could include more detail in the experimental section. What were the flow ratios in the DMA? Was an impactor used? What type of charge neutralizer was used? How was the data inverted? Was ... bars in Figures 1, 2, 3, and 5. If these data are not readily available it may at least be helpful to estimate the uncertainty based on the work of Rose et al. (2007).*

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All these issues have now been clarified in the text.

5. *Re Section 3.4: If 1800 cm<sup>-3</sup> deplete the vapor supersaturation disproportionately (to be noticed in the final size the instrument grows droplets) then I don't see how the maximum supersaturation in the instrument is not affected also. If true this would suggest a potentially serious problem for all studies that use the DMT instrument. This hypothesis needs corroboration from model calculations that compare the vapor flux to droplet growth rate. I did a very quick calculation assuming that 1800 droplets per cm<sup>-3</sup> grow instantaneously from 0 to 6 micron at 303.15 K and an environmental supersaturation of  $s = 0.5\%$ . If there is no vapor flux into the column the supersaturation drops to 0.48%. It therefore seems unlikely that the droplet growth is limited by sufficient supply of moisture.*

We thank the reviewer for pointing this out. We have revised the ammonium sulfate calibration and now is included in the revised graph. The SOA and sulfate aerosol exhibit similar activation kinetics.

*Furthermore, since the critical supersaturation of ammonium sulfate is lower than those for SOA, particles will activate earlier in the chamber and thus ammonium sulfate droplets should grow to larger sizes, even in the absence of kinetic limitations. I can offer two possible alternate explanations that may explain why the opposite behavior might have been observed 1) particles may evaporate between the exit of the column and sizing in the optical particle counter. The temperature of the optical block is usually elevated and can be set manually. Sometimes it is set to higher values to prevent fogging of the OPC. Perhaps this was the case during the calibration?*

The OPC was recalibrated and all activation kinetics curves match. The temperature of the OPC is always kept consistent, as the residence times, and temperature profiles.

2) *The final droplet size is also an indicator for the supersaturation inside the instrument. Is it possible that for the high supersaturations day-to-day variability of the achieved supersaturation can account for the differences?*

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The day-to-day variation is accounted for, as calibrations are carried out every day and are quite reproducible. Such results have been reported in all the publications using threshold droplet growth analysis (e.g., Sorooshian et al., 2008; Engelhart et al., 2008; Murphy et al., 2009; Asa-Awuku et al., 2009; Bougiatioti et al., 2009).

6. *I have a general comment about the application of the Szyskowski-Langmuir equation to CCN activity. The activation curves are well represent with a power law  $sc = !d^{-3/2}$ . If surface tension would be an effect there should be a deviation from this. How strongly will depend on the and parameter. To show that the Szyskowski- Langmuir equation applies it is necessary to show 1) how strongly the slope should deviate from the  $-3/2$  relationship, and 2) whether or not that can be seen given the uncertainties in the measurements. To my knowledge this has not been presented in the literature. In addition to this experimental question there are several theoretical points that are only partially discussed in the manuscript. The application of the Szyskowski-Langmuir isotherm obtained from bulk data in Kohler theory is questionable for the following reasons:*

1. *Partitioning may occur between the bulk and the surface of a curved droplet as was discussed by Li et al. (1998) and Sorjamaa et al. (2004).*

In cases where the aerosol is mostly organic, and soluble, the amount of mass can be sufficient for equilibrium partitioning. The reviewer does bring up a valid point; the implication is that the surface tension depression is lower than expected from assuming that the solute in the surface phase is negligible compared to the bulk droplet phase. You would still expect a concentration – surface tension depression dependence though, which for simplicity is assumed to follow the functional relationship of the Szyskowski-Langmuir isotherm. We have pointed this out in the text.

2. *Salting out may occur in the presence of some high molecular weight compounds as suggested in the manuscript. However, “salting out” seems thermodynamically tricky since it leads to an aqueous two phase system that is in thermodynamic equilibrium*

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(Albertsson, 1971). These aqueous two-phase systems have equal chemical potentials, i.e. water activities, but also have a clear interface. How “salting out” would occur in a curved droplet has not been theoretically explored and its effects on CCN activity are not understood.

We believe that there is a misinterpretation of “salting out”. We refer to enrichment in the surface phase of the droplet, not a phase separation in the bulk that would result in micelle formation. This has been reworded now.

3. Micelle formation may result in little variation with surface tension with carbon concentration as was also pointed out by Tabazadeh (2005).

Reference cited.

4. The surface tension of mixtures containing surface active and surface inactive species cannot be computed straightforwardly (Topping et al., 2005).

Indeed, but the cumulative impact on surface tension can be decoupled if two sets of CCN measurements are obtained: one where the hygroscopicity is dominated by inorganic solute (hence deviations from expected hygroscopicity is from the organic surface tension effect), and, one where organics dominates the hygroscopicity. Under such conditions, sufficient independent constraints on molar volume and surface tension can be obtained. And to date, all inferences on surface tension depression are of the 10% level, which is consistent with expectations from partitioning theory and most often less than levels obtained from direct measurements.

*For these reasons a rigorous application of surface tension in the framework of Kohler theory is difficult. Unless it can be shown that Szyskowski-Langmuir isotherms can be used to accurately predict CCN activity, including for mixtures as it has been applied to in this manuscript, the surface tension term in equation (3) remains a “free” parameter that is in fact adjusted to fit the measurement (i.e. the observed !). There is no reason to prefer one value of surface tension over another, since either density or molecular*

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*weight, or activity coefficients may counteract the effect of whatever value was chosen for the surface tension parameter.*

Surface tension has been applied to complex mixtures and provided reasonable agreement with measurements (Moore et al., 2008; Asa-Awuku et al., 2009, Engelhart et al., 2008 and King et al., 2009). One can argue that there is uncertainty in the measurements, but the combined molar volume-surface tension inferences are good enough for computations of CCN activity (especially since neglecting surface tension depression can lead to an “effective”  $\kappa$  that is considerably different from its true value). We do acknowledge however that inferring surface tension, is in the end, a parameterization based on a model applied to data. This does not reduce its utility, given that surface tension measurements of micron-sized droplets is challenging.

*While the above does not preclude the authors from presenting measured isotherms, which are needed to validate its applicability to measurements, I find it surprising that although no surface tension depression was measured (i.e. Figure 4), it was invoked later to explain the data.*

As stated in the text, insufficient material was present to make the direct surface tension measurements.

#### **Other comments:**

1. Equation (3) is in error, either the dry particle diameter is combined with the “B” parameter as was done in equation (4) or it should appear directly in equation (3).

We have made sure that the equations are consistent throughout the text.

2. The sentence that “the aerosol transition to pure AS with a  $m-1/2$   $i$  dependence implies that there are no strong surfactants” needs to be fixed. Do you mean “the hygroscopic behavior”? Also please add the Padro et al. reference which shows this point.

Done.

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