

Interactive comment on “Modeling the gas-particle partitioning of secondary organic aerosol: the importance of liquid-liquid phase separation” by A. Zuend and J. H. Seinfeld

Anonymous Referee #2

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Our ability to accurately replicate key processes that dictate gas/particle partitioning is still unclear. In this paper the authors perform a set of complex calculations to try and elucidate the role of liquid-liquid phase separation on gas/particle partitioning. The study is novel and it reaffirms the importance of complex thermodynamic phenomena at the single particle that requires additional studies before concrete conclusions can be made. Whilst the study is interesting there are some important issues that require clarification before the manuscript can be published. By using a more balanced view, in light of the current state of the science, I believe the paper will be further improved.

Major comments:

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Section 2.2.2, page 2207. It seems that important data is missing in this section that appears, in its present form, quite unbalanced. Contrary to line 7 on page 2208, evidence suggests there may be a strong physico-chemical argument for an increase in vapor pressure rather than, as the authors state, there being ‘no conclusive physico-chemical explanation’. It has been postulated by Chattopadhyay and Ziemann (2005) that keto substitutions in different positions on the C5 and C6 diacids both raise and lower vapor pressure. They suggest a carbonyl group in the 2-position hydrogen bonds to the carboxyl group, therefore reducing the strength of the intermolecular bonding and increasing vapor pressure. Perlovich et al. (2006) also see this same effect for OH groups adjacent to acid groups on the hydroxybenzoic acids, trends that seem to be supported by Booth et al (2010) and Froesch et al. (2010). Nannoolal et al (2004) and Nannoolal et al (2008) similarly note evidence where steric effects force an intramolecular hydrogen-bond which can raise the vapor pressure of the parent compound. Whilst raising the vapor pressure by adding extra groups might be counter intuitive, this behavior has clearly been seen in a number of systems measured using independent techniques and should not be discounted on the basis of a single set of data. Furthermore the authors comment on ‘recent measurements’ to support their approach using the same technique which contradicts all references given above. Based on the approach used in the current discussion, this leaves little justification for use of the EVAPORATION model without the empirical correction that Compernelle et al (2011) introduced in their original publication without a more balanced discussion. Might it be expected that the use of evaporation without this correction would give substantially different results in terms of the properties of the condensed phase and hence in terms of LLPS because of the differences in O:C ratio of the individual components? The authors do reference this critical dependence in the same section. It is for this reason I request the authors must therefore at least make a comparison between the effects of LLPS with and without the empirical correction if not to disregard the use of EVAPORATION without the correction entirely. The discussion in this section should at least be re-written to reflect the balanced state of evidence in the literature.

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Section 2.3. Here the authors comment how assuming a single mixed phase forces activity coefficients to become very large thus leads to out gassing. Does this mean the assumption of ideality in a single-phase droplet is 'better' than assuming non-ideality without phase separation? Is it likely that this assumption might hold for other degradation mechanisms?

In the same section the authors discuss how the O:C ratio of a mixture is a good proxy for determining the prevalence of LLPS. This appears to suggest that choice of 1) gas phase degradation model and 2) choice of vapor pressure predictive technique then is important for predicting this effect, which returns focus to the first discussion point.

Section 3. If the presence of LLPS is expected to significantly alter gas/particle partitioning, how sure are the authors that the reduced set of compounds chosen based on saturation vapor pressure alone would also represent the best set of compounds after LLPS is accounted for? This seems a bit circular. How much condensed mass would this reduced set represent relative to a 'full' simulation? Results in figure 1 look good, but how much mass is 'missing'? If you were to have a system of VOC degradation where a relatively large number of compounds represented a high proportion of the predicted condensed mass, would this mean the approach is somewhat limited? This seems a bit unclear.

Section 4.1.1 It is suggested that tuning a degree of dimer formation improves comparisons with measurements of mass loading. Is there a reasonable value of the dimerization parameter that would improve predictions of one-phase calculations?

Minor comments

Page 2002, line 10: Might be useful to include the reference to S. L. Clegg, J. H. Seinfeld and P. Brimblecombe (2001) Thermodynamic modeling of aqueous aerosols containing electrolytes and dissolved organic compounds. *J. Aerosol Sci.* 32, 713-738.

Page 2221 line 19: The authors state "probably lens-shaped phase on a largely aque-

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ous organic-inorganic droplet." Evidence must be provided to support this.

Page 2229 line 2: Please correct the term "highly super-linearly"

References: Chattopadhyay and Ziemann, *Aerosol Sci. Tech.*, 39, 1085–1100, 2005. Froehner et al., *ACP*, 10, 5873-5890, 2010. Nannoolal et al, *Fluid Phase Equilib*, 226,45-63,2004. Nannoolal et al, *Fluid Phase Equilib*, 269,117-133,2008. Perlovich et al. *J Pharm Sci*, 95, 1448-1458, 2006.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 12, 2199, 2012.

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