

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

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The authors would like to thank Referee #2 for the careful review of the manuscript and valuable comments. We address the reviewer’s comments in our point-by-point response given below. We will incorporate corresponding changes and clarifications in a revised version of the manuscript.

Major comments

Referee #2: Section 2.2.2, page 2207. It seems that important data is missing in C1107

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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 physicochemical 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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Author's response: We will extend our discussion on the use of the EVAPORATION model without the empirical correction term affecting functionalized dicarboxylic acids. This will provide a more balanced view on the current state of knowledge, as suggested by this reviewer. We have a number of good reasons to reject the use of the functionalized diacid correction in the EVAPORATION model, explained in the following.

The reviewer points out that there is a possible physicochemical explanation for raised vapor pressures of substituted dicarboxylic acids. We agree, yet there are additional important facts to consider. Chattopadhyay and Ziemann (2005) found that keto substitutions in α -position of a carboxyl group can raise the solid state vapor pressure of dicarboxylic acids, while keto substitutions at a β -position or further away from the carboxyl group, lower the solid state vapor pressure. For example, in case of glutaric acid (pentanedioic acid) they found an increase of the vapor pressure by less than one order of magnitude for 2-oxopentanedioic acid at 298 K, yet a decrease in vapor pressure by more than one order of magnitude for 3-oxopentanedioic acid. As mentioned by the reviewer, it is suggested by Chattopadhyay and Ziemann (2005) that a keto group in the α -position may hydrogen-bond with the carboxyl group. Hence, an internal hydrogen bond may reduce the intermolecular bonding and may lead to an increase in vapor pressure relative to the value of the unsubstituted parent dicarboxylic acid (this is a possible physicochemical reason). Using a different experimental technique, Booth et al. (2010) do not find the effect reported by Chattopadhyay and Ziemann (2005) for the solid state vapor pressures of keto-substituted glutaric acid at 298 K, rather they find a slight decrease in vapor pressure due to the substitutions – although the reduction is smaller than what would be expected from a simple group additive model. In case of 2,3-dihydroxy succinic acid (tartaric acid), an increase in solid state vapor pressure with respect to succinic acid is reported by Booth et al. (2010). Booth et al. (2010) use thermochemical data (enthalpy and entropy change of fusion, melting point) to infer subcooled liquid vapor pressures from their measurements of solids. For several substituted dicarboxylic acids, they report a

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

substantial increase in subcooled vapor pressure relative to the parent compounds, in some cases by more than one order of magnitude and in several cases against the trend of the corresponding solid state values. Part of these unexpectedly high liquid state vapor pressure values reported by Booth et al. (2010) may be due to significant uncertainties in the thermochemical data used for the solid-to-liquid state conversion. The important point here concerns the physical state: an increase in vapor pressure due to hydroxyl or ketone substitutions of dicarboxylic acids has been found only in experiments referring to measurements of the solid state vapor pressure – and not in a single case for liquid (subcooled) samples. But it is the vapor pressure referring to the liquid state, which is predicted by EVAPORATION and which is the reference state for gas-particle partitioning calculations. Contrary to what the reviewer stated, Frosch et al. (2010) report a decrease by about one order of magnitude for the vapor pressure of keto-substituted glutaric acid and their measurements likely refer to the liquid state. Recent experiments by Huisman et al. (2012, paper in review), using the electrodynamic balance technique of Soonsin et al. (2010) for direct measurements of liquid state vapor pressures, show for several substituted di- and tricarboxylic acids a clear decrease of the subcooled liquid state vapor pressure, for which Booth et al. (2010) reported an increase.

As stated in Section 2.2.2., Compernelle et al. (2011) implemented an empirical correction term in EVAPORATION in order to account for the findings of Booth et al. (2010) (the unexpectedly high subcooled liquid vapor pressures), since otherwise EVAPORATION could not reproduce such effects. EVAPORATION includes a “regular” second order correction parameter to account for the effect of a ketone group in α -position to a carboxyl group, but this parameter cannot account for the (apparent) large increase in vapor pressure of substituted diacids. Furthermore, the implementation of the correction term in EVAPORATION applies to all compounds with at least two carboxyl groups and at least one additional hydrogen-bonding or carbonyl-like group (Compernelle et al., 2011). Hence, this includes compounds with a ketone group in the β -position (and further away), for which no measurement indicates an increase in

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

vapor pressure. We argue that this state of knowledge provides sufficient reasons to reject the empirical correction term in the EVAPORATION model.

In addition, we note that only one compound of the α -pinene SOA products in the current study, the ESTER_dimer (see Table 1), would be affected by the empirical correction in EVAPORATION. In case of the ESTER_dimer, a ketone and an ester functionality are present in addition to two carboxyl groups, but neither of these groups is in α -position of a carboxyl group. Besides, the ESTER_dimer makes up only a small fraction of the predicted SOA.

In summary, using EVAPORATION without the correction term is supported by the current state of science and clearly the better choice for the system used in the study.

Manuscript revision: We suggest adding the following statements in the revised manuscript.

Page 2208, line 3, before “Compernelle”: “In case of vapor pressure measurements referring to the solid state, Chattopadhyay and Ziemann (2005) found that keto substitutions in α -position of a carboxyl group can raise the solid state vapor pressure of dicarboxylic acids with respect to the unsubstituted parent dicarboxylic acid, while keto substitutions at a β -position or further away from the carboxyl group, lower the solid state vapor pressure. For example, in case of glutaric acid (pentanedioic acid) they found an increase of the vapor pressure by less than an order of magnitude for 2-oxopentanedioic acid at 298 K, yet a decrease in vapor pressure by more than an order of magnitude for 3-oxopentanedioic acid. Chattopadhyay and Ziemann (2005) suggest that a keto group in the α -position may hydrogen-bond with the carboxyl group. Hence, an internal hydrogen bond may reduce the intermolecular bonding and may lead to an increase in vapor pressure relative to the value of the unsubstituted parent dicarboxylic acid. However, such effects of vicinal functional groups in multifunctional compounds have been found only for vapor pressure measurements of samples in the solid state, while measurements of samples in the liquid state report a decrease in vapor pressure with additional ketone or hydroxyl functionalities (Frosch et al., 2010; Huisman et al., 2012). The liquid (subcooled) state vapor pressure data of

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Booth et al. (2010) is obtained via a thermodynamic phase state conversion from the measurements in the solid state. Uncertainties in thermochemical data used in the phase state conversion may be partly responsible for the unexpectedly high subcooled liquid vapor pressures reported by Booth et al. (2010)."

Page 2208, line 6: The sentence "However, there is no conclusive physicochemical explanation for such an effect in functionalized diacids and higher acids." is replaced by "However, the current state of knowledge suggests that the empirical correction in EVAPORATION is in disagreement with all corresponding vapor pressure data measured for the liquid (subcooled) state.

Page 2208, line 10: "... a lowering of the vapor pressures ..." replaced by "... a relative decrease in (subcooled) liquid state vapor pressures...".

Page 2208, line 13: We add: "In addition, we note that only one compound of the α -pinene SOA products in the current study, the ESTER_dimer (see Table 1), would be affected by the empirical correction term in EVAPORATION."

Referee #2: 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?

Author's response: As is stated in the article (e.g., page 2225 line 8 - 13), we do not recommend either assumption. Keeping that in mind, we answer these questions from the forced one-phase perspective. In a forced one-phase calculation, assuming ideality may be better at low RH and lower organic:inorganic ratios, while the assumption of non-ideality is likely better at higher RH and for high organic:inorganic ratios (see Fig. 5, panels (a) - (c)). Regarding the effects of significant (potentially complete) salting-out of organics to the gas phase in the forced one-phase case with consideration of non-ideality, assuming ideal mixing is a "safer bet", but will significantly overpredict organic PM mass. Based on the group-contribution concept

with AIOMFAC, these assumptions will hold for other SOA + salt systems from other degradation mechanisms. As discussed on page 2210, a first-order assumption based on the O:C ratio (as a proxy for polarity) would suggest that the higher the (average) O:C of SOA, the better the agreement will become with a forced one-phase case including non-ideality. However, at high RH, an ideal mixing assumption will also tend to agree better with the “true” equilibrium solution in case of SOA of higher average O:C.

Referee #2: 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.

Author’s response: The MCM-EVAPORATION-AIOMFAC approach is a coupled model; all three specialized models involved have an impact on the overall results, which includes the prediction of a potential LLPS in a system. The existence of an LLPS or a single liquid phase for a “given” overall PM mixture is determined with an algorithm based on AIOMFAC activities only, but the different compounds and their abundances in the overall PM mixture are, of course, also influenced by the predicted distribution of SOA species and their pure compound vapor pressures. The O:C ratio of a mixture as a proxy for the prevalence of a LLPS is, e.g., also the basis for the LLPS-parameterization by Bertram et al. (2011).

Referee #2: 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?

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

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.

Author’s response: We assume by “figure 1” the referee actually refers to Fig. 3. The compounds are chosen based on saturation vapor pressure alone, because the saturation vapor pressure of an organic compound sets the scale: orders of magnitude impact of vapor pressure vs. approximately up to one order of magnitude effect of non-ideality. Unless a VOC or IVOC compound is extremely abundant in the gas phase, the partitioning to the particle phase is negligible. An example for an extremely abundant volatile compound that partitions significantly to the condensed phase is water. No VOC or IVOC is nearly as abundant in the atmosphere relative to its saturation vapor pressure. Furthermore, allowing an LLPS to exist has the effect of moderating the apparent influence of non-ideality, i.e., keeping the activity coefficients closer to unity. A comparison of Figs. 2a and 4d-e shows that the most volatile species present in our system of α -pinene degradation products (e.g. C109OOH) are virtually only present in the gas phase (also shown in Fig. 6). Thus, excluding the more volatile VOC and IVOC species from our partitioning calculations is well justified and the “missing” mass is negligible. Whether a high number or low number of compounds represents a high proportion of the predicted PM mass has no influence on our approach of selecting the system species by saturation vapor pressure.

Referee #2: 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?

Author’s response: The tuning parameter λ , accounting for a degree of possible dimer formation, is set based on the comparison to the chamber data shown in Fig. 3. Hence, the parameter is set based on one-phase calculations. Since the dimers

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considered in the system are low-O:C compounds, in a hypothetical forced one-phase calculation with non-ideal mixing, the activity coefficients of the dimers will be much larger than unity (in the presence of sufficient amounts of ammonium sulfate ions), making the tuning of the (lacking) PM mass by means of a higher degree of dimer formation nearly impossible.

Minor comments

Referee #2: 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.

Author's response: We add the reference as suggested (on page 2202).

Referee #2: Page 2221 line 19: The authors state “probably lens-shaped phase on a largely aqueous organic-inorganic droplet.” Evidence must be provided to support this.

Author's response: We revise this sentence slightly and provide a reference.

Manuscript revision: Page 2221, line 17 - 19, we modify the statements to: “... and considering the much higher water-content of phase α , phase β will only form a relatively small phase, probably lens-shaped or as a thin coating (Reid et al., 2011), on a largely aqueous organic-inorganic droplet.”

Referee #2: Page 2229 line 2: Please correct the term “highly super-linearly”

Author's response: Fragment revised: “highly super-linearly” replaced by “super-linearly”.

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