Atmos. Chem. Phys. Discuss., 12, C1097–C1106, 2012
www.atmos-chem-phys-discuss.net/12/C1097/2012/

Atmospheric
Chemistry
and Physics
Discussions

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

A. Zuend and J. H. Seinfeld

zuend@caltech.edu

Received and published: 29 March 2012

The authors would like to thank Referee #1 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.

Comments

Referee #1: 1. Page 2224. Holding the ammonium sulfate mass concentration constant in the simulations of high, moderate, and low SOA loading has the effect of varying the fraction of organic:inorganic (which is stated by the authors, P. 2224 lines 17-18). The higher ratio of organic: inorganic in the high loading experiments lessens the importance of non-ideal interaction between the organic and inorganic phases (also stated on P. 2224: “the influence of organic – ion interaction is diminished”). Could the authors comment on the effects of varying the organic:inorganic fractions at one mass loading (i.e., the loading and organic:inorganic fractions are co-varied in present study)? If the organic:inorganic were held constant, would the accuracy of the forced 1-phase case be highest for the low loading system (highest O:C modeled), as phase mixing is expected to increase with increasing O:C?

Author’s response: Our choice of holding the ammonium sulfate mass concentration constant is based on the idea that in the ambient air organic:inorganic ratios also vary as organic loading levels change. This reflects a situation of uncorrelated sources of ammonium sulfate and SOA from biogenic precursors. The statement cited by the referee (P. 2224 lines 17-18) “the influence of organic $\leftrightarrow$ ion interaction is diminished” refers to the salt-effect in the forced 1-ph. case. At 60% RH and 298 K, the equilibrium case calculations predict the following mass fractions of ammonium sulfate in the dry (water-free) overall PM mixture, mf$_d$(AS): ~ 0.108, ~ 0.349, and ~ 0.766, for high, moderate, and low SOA loading, respectively. At higher ratios of organic:inorganic mass fractions (lower values of mf$_d$(AS)), the forced 1-ph. case agrees better with the results from the equilibrium case, because the salting-out effect is less pronounced for the reasons discussed on P. 2224. Additional calculations using approximately the same organic:inorganic dry mass ratio for the low loading case as was found in the high loading case, i.e., mf$_d$(AS) $= \sim 0.108$ (organic:ammonium sulfate mass ratio of ~ 8.27), result in a similar behavior in the low loading case. That is, the relatively small amount of ammonium sulfate in the forced 1-ph. case does not cause partitioning of all organics to the gas phase at lower RH, as was found at the higher mf$_d$(AS) $= \sim 0.766$ used in the study. The additional calculations also support the assumption of the reviewer that the accuracy (agreement) of the forced 1-phase case

with the equil. case is highest for the low SOA loading system (highest O:C modeled), as phase mixing is expected to increase with increasing O:C. However, it is important to note that these are hypothetical results in the sense that in reality (if the model is reasonably accurate) the salt-content would be high enough (at both the low and high organic:inorganic ratios) to cause a liquid-liquid phase separation.
Manuscript revision: Page 2224, line 24, the following statements will be added:
"Note that in the forced 1-ph. case effects of non-ideal mixing are mainly controlled by the "dry" ratio (water-free basis) of organics:inorganics, this includes the extent to which the organic compounds are salted out to the gas phase. At $60\,\%$ RH and 298 K, the equilibrium case calculations predict the following mass fractions of ammonium sulfate in the dry (water-free) overall PM mixture, mf$_d$(AS): $\sim\ 0.108$, $\sim\ 0.349$, and $\sim\ 0.766$, for high, moderate, and low SOA loading, respectively. At higher ratios of organic:inorganic mass fractions (lower values of mf$_d$(AS)), the forced 1-ph. case agrees better with the results from the equilibrium case, because the salting-out effect is less pronounced. For example, if in a calculation the amount of ammonium sulfate is highly reduced in the low SOA loading system to match the dry organic:inorganic ratio of the high SOA loading system, i.e., mf$_d$(AS) $=\ \sim\ 0.108$ (organic:ammonium sulfate mass ratio of $\sim\ 8.27$), the results of the forced 1-ph. case agree much better with the equil. case. However, in atmospheric aerosols the ratio of organic:inorganic components is neither constant nor generally known, so that forcing a single liquid phase may be reasonable only under certain conditions, which depend on mf$_d$(AS) as well as the miscibility of the organic fraction with aqueous inorganic ions."

Referee #1: 2. Page 2212 line 1 - 18: The parameterization used by Bertram et al., 2011 is based on a purely empirical relationship (with discussion of organic molecule polarity as a factor in phase separation or mixing). Can your benchmark model say anything additional regarding the thermodynamics that would support their parameterization?
Author's response: As discussed on page 2212, in the applicable range of organic-

to-sulfate mass ratios, the parameterization by Bertram et al. (2011) is a function of organic O:C ratio only. When according to the parameterization a LLPS is predicted, the LLPS is assumed to be a complete organic/electrolyte phase separation. Hence, in a phase diagram plotted as RH (y-axis) vs. dry composition (x-axis), the LLPS onset is predicted to be a horizontal line (in the applicable organic-to-sulfate range). Our thermodynamic phase separation model based on AIOMFAC can be used to test whether or not such a "horizontal binodal curve" is a good assumption for a given system (given the model is reasonably accurate). In case of the alpha-pinene SOA + water + ammonium sulfate system, the model predicts a near-horizontal binodal curve over a wide range of org:sulf ratios and that virtually complete phase separation is reached relatively close below the LLPS onset. Hence, in this case, the assumptions underlying the parameterization of Bertram et al. (2011) are supported. In other cases, especially for systems with higher average O:C ratios, the LLPS may be incomplete and the curvature of the binodal more important, as e.g. shown by Song et al. (2012).

Referee #1: 3. Page 2217 line 6 - 10: This system is at 40% RH and the authors describe this as salt-free aqueous organic mixture, yet in Section 4.2, page 11 - 17, the authors state that the RH range 30% to 99% can be assumed to be a liquid PM phase containing inorganic ions. These two statements should be clarified. This is due to the solid seed used in the 40% RH chamber experiments, but should be clarified.
Author's response: This is a point also mentioned by referee #3 and we refer the reader to our reply to referee #3 for a more detailed discussion. We will clarify the reasonable assumption of a salt-free system in the presence of a solid ammonium sulfate seed at $40\,\%$ RH in the revised manuscript.

Referee #1: 4. Page 2217-2218: Good agreement is found between the model and experimental chamber data for mass yield, but because dry seed was used, no treatment of phase separation was needed, and consideration of ideal vs. non-ideal behavior was also not a large influence on the model results. (P. 2217 line 10 "For such a salt-free aqueous organic mixture, the model predicts a one-phase state as the equilibrium PM-state for all models"; P. 2218 line 21: "non-ideality is not an important factor in the salt-free case"). The main conclusions of the manuscript are that both non-ideality in the condensed phase and phase separation as a consequence of non-ideal behavior need to be considered for accurate modeling of SOA composition and mass (P. 2200 lines 23-25), while the main result of the comparison to chamber data seems to be validation of the accuracy of the MCM v3.1 and EVAPORATION, with no treatment of phase separation. The purpose of the comparison to chamber data (it demonstrates excellent prediction of PM mass for a 1-phase organic system) should be made clearer to the reader.

Author's response: On page 2218, line 19 - 24 it is stated in the article: "The agreement between predicted and measured SOA yields is a remarkable demonstration of the applicability of the MCM-EVAPORATION-AIOMFAC modeling approach. Since non-ideality is not an important factor in the salt-free case here, it means that the species and amounts predicted by MCM v3.1 as well as the vapor pressures predicted by EVAPORATION are very good estimations, as they constitute the main impact on the model results."

We also state on that page that consideration of non-ideality becomes important at higher RH in the salt-free system. The referee is correct in that the comparison of the model to chamber data is mainly a validation of the accuracy of MCM v3.1 and EVAPORATION, and we will further clarify this in the revised manuscript. However, the comparison also shows that the consideration of non-ideality by AIOMFAC is reasonable in the salt-free system. If, for some reason, AIOMFAC would predict large effects of non-ideal mixing in the salt-free system, then this would also affect the modeled yields and become visible in Fig. 3.

Manuscript revision: Page 2218, line 21 - 24, we modify the statements to: "Since non-ideality is not an important factor in the salt-free case at 40 % RH, it means that the species and amounts predicted by MCM v3.1 as well as the vapor pressures

predicted by EVAPORATION are very good estimations, as they constitute the main impact on the model results. Hence, the comparison of the model results to chamber data provides mainly a validation of the accuracy of MCM v3.1 and EVAPORATION for an aqueous organic one-phase system."

Referee #1: 5. Page 2221 line 18 - 19: Provide a reference for the statement "probably lens-shaped phase on a largely aqueous organic-inorganic droplet."

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 #1: 6. Page 2233 line 6 - 8: Provide reference from atmospheric aerosols.

Author's response: To our knowledge, there are no direct observations of LLPS in atmospheric aerosols because this constitutes a technical challenge (and not necessarily because they are not present). Hence, we have no observational proof for this statement and reformulate it to indicate the speculative nature of this point.

Manuscript revision: Page 2233, line 6 - 8, we modify the statement to: "Based on the computational results for the aqueous α-pinene + ammonium sulfate SOA system and the group-contribution concept of our model, it is highly probable that SOA of moderate or lower average O : C ratio will cause LLPS in the presence of aqueous inorganic ions. Given the abundance of organic aerosol of moderate or lower average O : C in the troposphere (e.g., Aiken et al., 2008; Ng et al., 2010), it is reasonable to assume that such phase separations are a prevalent feature of atmospheric aerosols over a wide range of RH, aerosol loading, and temperature."

Minor comments

Referee #1: Page 2200 line 7: AIOMFAC and EVAPORATION acronyms should be defined.
Author's response: The acronyms of the models AIOMFAC and EVAPORATION are given at their first occurrence in the main text. In the Abstract (Page 2200) the following is written: "We introduce a novel combination of the thermodynamic models AIOMFAC (for liquid mixture non-ideality) and EVAPORATION (for pure compound vapor pressures) ...". From that it is clear that the acronyms refer to thermodynamic models and what they are used for. Also, since these models are better known by their acronyms than by their full name, we prefer to keep it way it is done now in the Abstract.

Referee #1: Page 2200 line 16: replace "different" with "several"
Author's response: Suggested replacement made in the revised manuscript.

Referee #1: Page 2200 line 18 - 20: Awkward sentence, perhaps replace "Both" with "By"
Author's response: Sentence modified.
Manuscript revision: Page 2200 line 18 - 20, modified sentence: "It is shown that forcing a liquid one-phase aerosol with or without consideration of non-ideal mixing bears the potential for vastly incorrect partitioning predictions.“

Referee #1: Page 2200 line 21: Replace "at high RH by more than 200%" with "by more than 200% at RH values of X%"
Author's response: Sentence revised.
Manuscript revision: Page 2200 line 20 - 21, modified sentence: "Assuming an ideal mixture leads to substantial overestimation of the particulate organic mass, by more than $100\,\%$ at RH values of $80\,\%$ and by more than $200\,\%$ at RH values of $95\,\%$."

Referee #1: Page 2202 line 16: Reference Koop et al., 2011 and Poschl et al., 2011
Author's response: These are our own thoughts and statements, no references necessary.

Referee #1: Page 2202 line 28: Remove Lienhard et al., 2012 as it has not yet been published
Author's response: Lienhard et al. (2012) has been published recently.

Referee #1: Page 2211 line 19: Insert comma after "computations"; Insert comma after "allowed"
Author's response: In the revised version, we insert a comma after "Note that" and after "computations".

Referee #1: Page 2214 line 21: replace "of" with "from"
Author's response: Fragment "of the dark α-pinene ozonolysis" replaced by "from the dark ozonolysis of α-pinene".

Referee #1: Page 2218 line 13: define "these conditions" are you referring to low PM mass concentration or high PM mass concentrations
Author's response: Sentence revised: "these conditions" replaced by "at $40\,\%$ RH in the salt-free system".

Referee #1: Page 2222 line 11-13: Awkward sentence - "For example, the bar graphs in the bottom panels of Fig. 4 show how PINIC partitions predominantly to the PM phase at high loading, is mostly found in the PM phase at moderate loading (80 %),

but only to about 40% in the PM at low loading." Consider changing to - "For example, the bar graphs in the bottom panels of Fig. 4 show how PINIC partitions predominantly to the PM phase at high loading, is mostly found in the PM phase at moderate loading (80 %), and is found in substantial amounts in both the PM and gas phases at low loading (40% in PM phase)."
Author's response: Sentence revised as suggested.

Referee #1: Page 2229 line 2 – 3: Use a better phrase than "highly super-linearly"
Author's response: Fragment revised: "highly super-linearly" replaced by "super-linearly".

References

- Bertram, A. K., Martin, S. T., Hanna, S. J., Smith, M. L., Bodsworth, A., Chen, Q., Kuwata, M., Liu, A., You, Y., and Zorn, S. R.: Predicting the relative humidities of liquid-liquid phase separation, efflorescence, and deliquescence of mixed particles of ammonium sulfate, organic material, and water using the organic-to-sulfate mass ratio of the particle and the oxygen-to-carbon elemental ratio of the organic component, Atmos. Chem. Phys., 11, 10995–11006, doi:10.5194/acp-11-10995-2011, 2011.
- Lienhard, D. M., Zobrist, B., Zuend, A., Krieger, U. K., and Peter, T.: Experimental evidence for excess entropy discontinuities in glass-forming solutions, J. Chem. Phys., 136, 074515, doi:10.1063/1.3685902, http://link.aip.org/link/?JCP/136/074515/1, 2012.
- Ng, N. L., Canagaratna, M. R., Zhang, Q., Jimenez, J. L., Tian, J., Ulbrich, I. M., Kroll, J. H., Docherty, K. S., Chhabra, P. S., Bahreini, R., Murphy, S. M., Seinfeld,

J. H., Hildebrandt, L., Donahue, N. M., DeCarlo, P. F., Lanz, V. A., Prévôt, A. S. H., Dinar, E., Rudich, Y., and Worsnop, D. R.: Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry, Atmos. Chem. Phys., 10, 4625-4641, doi:10.5194/acp-10-4625-2010, 2010.
- Reid, J. P., Dennis-Smither, B. J., Kwamena, N.-O. A., Miles, R. E. H., Hanford, K. L., and Homer, C. J.: The morphology of aerosol particles consisting of hydrophobic and hydrophilic phases: hydrocarbons, alcohols and fatty acids as the hydrophobic component, Phys. Chem. Chem. Phys., 13, 15559–15572, doi:10.1039/C1CP21510H, 2011.
- Song, M., Marcolli, C., Krieger, U. K., Zuend, A., and Peter, T.: Liquid-liquid phase separation and morphology of internally mixed dicarboxylic acids/ammonium sulfate/water particles, Atmos. Chem. Phys., 12, 2691–2712, doi:10.5194/acp-12-2691-2012, 2012.

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