Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-344-RC1, 2019

Atmospheric Chemistry and Physics
Discussions

Interactive comment on “Effects of Water-soluble Organic Carbon on Aerosol pH” *by* Michael A. Battaglia Jr. et al.

Anonymous Referee #1

Received and published: 10 June 2019

This article by Battaglia, Weber, Nenes and Hennigan explores effects of water-soluble organic compounds on aerosol acidity by means of thermodynamic modeling. Two data sets from field measurements distinct by acidity (Baltimore & Beijing) are used to provide information about inorganic constituents, aerosol mass concentration and the water-soluble organic fraction. The authors provide new insights into the effects of organic compounds on aerosol water content and the activity coefficient of H+. This topic is of interest for the atmospheric chemistry community, since aerosol acidity has been linked to a range of chemical and physical properties of particulate matter, but relatively few studies have attempted to quantify the effects of organic/inorganic mixing on aerosol pH. While certain effects of inorganic/organic aerosol mixing have been excluded in this work, e.g. liquid-liquid phase separation and lower relative humidity

conditions, the study by Battaglia et al. provides interesting findings for single-phase aqueous aerosol by using a combination of state-of-the-art thermodynamic models. It is shown for the cases studied that the pH is largely controlled by the inorganic aerosol species, which is in agreement with other related studies (Pye et al., 2018).

The manuscript is generally well structured and provides a good introduction about the need for understanding the effects of organic acids and non-acids on pH. However, the descriptions lack some details with regard to the methods employed and would benefit from additional discussion about the choice of a rather limited number of specific organic non-acids and dicarboxylic acids and how these may affect the simulation results.

I am in support of the publication of this work after my minor points on methods and assumptions have been addressed by the authors. General and specific comments are provided below.

1 General comments

1. Factorial design method (pages 8, 9).
   A factorial modeling experiment design was used to represent different combinations and concentration levels of organic compounds. Since this is not a widespread approach used by atmospheric chemists, it would be adequate to provide a better description of what was done exactly and why. For example, on page 9 is stated: “*. . . and combined in factorial fashion: each organic acid concentration level combination of the three organic acids, and vice versa for the non-acid organic species. Combinations of organic acids and non-acid organic species were not explicitly considered here.*”
   This could be phrased much better for clarity and perhaps an example could be provided to make clear what is meant (e.g. that the approach involves indepen-

dent combinations, rather than permutations) and what is "factorial" about this method. Also, references to adequate literature describing this approach are missing.

2. Liquid-liquid phase separation (LLPS).
   Phase separation was not considered in the calculations from this study, but the topic is discussed in the introduction, which is valuable. It is well-known that non-ideal mixing in organic/inorganic solutions can cause LLPS, as the authors also point out. However, what remains unclear is how the authors concluded that their cases are not affected by phase separation. Page 8, line 8 – 12: "*The RH in all simulations was fixed at either 70%, 80%, or 90%, with inorganic system inputs calculated and invariant at each RH level based on the initial input data from either Baltimore or Beijing to ensure deliquescence of inorganic aerosol particles, to understand the sensitivity of the model-predicted aerosol pH to changes in RH (ALW), and to avoid liquid-liquid phase separation as a potential cause of organic-influenced aerosol pH changes (Pye et al., 2018).*"
   It should be clarified how avoiding LLPS is related to deliquescence of inorganic particles. How sure are the authors that LLPS would not occur, say at 70% RH, in their systems when high amounts of organics are present? Was this checked quantitatively? For example, the authors could confirm that organic activity coefficients remain less than $\sim$ 5 – 10, since studies like Donahue et al. (2011, https://doi.org/10.5194/acp-11-3303-2011) suggest that "Somewhere between $5 < \gamma < 10$ phase separation becomes very likely". The LLPS constraints from You et al. 2013 (mentioned much later on page 19) could also be useful for the discussion in this context.

3. Acids vs. non-acid organics.
   In the abstract and similarly on page 18, line 19, it is stated that "*surprisingly, non-acidic WSOC compounds were found to have a larger effect on pH than organic acids owing to their stronger impacts on* $\gamma_{\mathrm{H+}}$". It is not made clear what

is *surprising*, please clarify. Also, how robust is this result given the choice of rather small, polar and hygroscopic organic diacids in this study. Would the same explanation hold true if a diacid of lower O:C ratio (less hygroscopic) were used? Moreover, the finding may depend on how ISORROPIA, E-AIM, UNIFAC and AIOMFAC treat organic acids (accounting for dissociation or not); see specific comments.

2 Specific comments

- Page 2, line 23: define the meaning of "*aerosol strong acidity or total acidity*"
- P3, l6: "*to obtain the pH of an aerosol distribution*". Since distribution is mentioned, would the same pH be expected for all aerosol particles over a considerable size range (e.g. ultrafine vs. larger accumulation mode particles)? Do the input data from measurements account for size modes?
- P3, l10 - 15: the aerosol thermodynamic models are introduced. At this point it is appropriate to define the acronyms and to cite the key references describing the models, which are missing; see associated websites. Also, citing Ganbavale et al. (2015) in the context of AIOMFAC and its web model seems inadequate as that study does not concern organic-inorganic mixtures.
- Pages 3 and 4 (first paragraph): AIOMFAC is discussed as only being an activity coefficient model, which seems correct, but the authors forgot to mention that there are equilibrium models based on AIOMFAC, including the one used by Pye et al. (2018), Hodas et al. (2015), Zuend et al. (2010, 2012) and others. The study by Pye et al. used both ISORROPIA and AIOMFAC-based equilibrium models to estimate aerosol pH. It seems that the authors only refer to the online model of AIOMFAC, which could be made clear. Also, do ISORROPIA, E-AIM,

AIOMFAC solve the ion association/dissociation equilibria, like bicarbonate and bisulfate in aqueous systems? What about organic acid dissociation? There is an E-AIM model version for specific acids, but it seems that organic acid dissociation is not considered explicitly by the models, right? Discussion of this could be important for pH calculations in the context of diacids (of different pKa values) and when contrasting the effects of acidic vs. non-acidic organics.

- P4, l 15: Define LLPS
- P5, l 5: Rephrase “increasing particle phase partitioning”; what kind of partitioning is meant? gas-particle, liquid-liquid?
- P6, l12: Rephrase “S-curves” - these are known as sigmoid curves.
- P6, l16: how was the threshold uncertainty of 0.5 pH units determined? Cite a reference.
- P8, l18: What is “the standard table of AIOMFAC organic species”? this is unclear
- P10, l9: Clarify meaning of “Metastable mode” in this context. This seems to be a technical term used with ISORROPIA, but jargon should be avoided.
- P11, l16: “*The selected species and order of allocation of the ionic species appears to be dependent solely on the researcher, and a priori knowledge of which molecular species are likely to exist in the aerosol particle as the dissociated ionic species.*” It is unclear what a priori knowledge is needed. Do the authors mean that the choice of species allocation affects model predictions or not?
- P17, l1 - 4: The statements in this sentence appear to contradict each other. Is the increase of oxalic acid from 1 to 2 μg/m^3 not a discrete increase in concentration? Revise.

- P17, l9 - 11: “*Taken together, this may indicate that the system pH changes to such a point that one of the acids which may not previously have been fully dissociated begins to do so, spontaneously lowering system the pH by nearly 0.4 pH units*”. Are you referring to inorganic acids here or to the dicarboxylic acids? If the latter, is AIOMFAC even computing the dissociation of acids (explicitly or implicitly)?
- P18, l10: rephrase
- P19, l5: “*the situation becomes more complicated as there exists no accepted definition of pH for a predominantly-organic phase in which the solvent is the organic aerosol constituents rather than ALW.*”
  This referee considers this statement to be incorrect. Isn’t the definition by IUPAC the accepted definition of pH, which was also used in this study? The definition of pH by IUPAC seems to be applicable in either situation; it solely depends on the H+ activity. Further, any (organic) phase containing dissolved H+ likely also contains some amount of water.
- P19, l10: Didn’t Pye et al. (2018) consider also cases with a single aqueous phase? Their Figure 3 suggest they had both LLPS and single phase cases for the SOAS field study.
- P21, l15: It is unclear how a “forced metastable condition” would help to avoid LLPS. These are two independent processes/states. Clarify.
- P22, l20: “for especially glassy aerosols” – unclear how viscosity and glassy aerosols are related to pH in this context. Glassy aerosols would indicate significant equilibration time scale effects, but what does that have to do with pH?
- P23, l4: While the authors show that the aerosol pH value is mostly determined by inorganic species, the present study and previous work cover a relatively limited

set of organics compounds and conditions. Hence, general conclusions should be stated carefully. One aspect that warrants further study and discussion concerns the partitioning of organic acids that may dissociate significantly at relatively high pH (say > 4) as well as the effects of amines acting as bases similar to ammonia. Therefore, it may be premature to conclude that exclusion of organics for future aerosol pH predictions is always justified. A disclaimer in that context may be appropriate.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-344, 2019.