

Response to Reviewers Comments

I.R. Zamora and M.Z. Jacobson

We would like to thank the reviewers for taking the time to carefully read the manuscript, and provide helpful comments. We appreciate the opportunity to improve our paper by incorporating their feedback. The comments for Reviewers 1 and 2 are addressed in the manuscript text as indicated below each comment.

Reviewer 1

The work presents a systematic study, and parameterisation of, water activity measurements for mixed systems of humic-like substances, diacids and sugars. It then extends the work to include an inorganic fraction. Modeling these systems using the ZSR equation they found it started to break down for multicomponent mixtures. I recommend that this work is published in ACP, provided that the following comments are addressed:

1. In section 2.1 you say the solutions were stirred until homogenous. Was all the material going into solution or was some of it just suspended?

There was indeed some suspended solid visible on the solutions at higher concentrations. To clarify this point, we have modified the first sentence and added an additional sentence to section 2.1 as follows:

“Solutions were prepared by weighing each solid component and water onto a glass vessel, then stirring until the solution became as homogeneous as possible. Note that some suspended solid was visible on the solutions at higher concentrations, indicating that not all of the solid went into solution.”

2. pg 1-57 ln4 you mention that due to the low solubility of succinic acid, a wide range of mass fractions wasn't explored. Why didn't you use malonic or glutaric acid instead as your category 2 compound? They are far more soluble (odd-even effect).

In spite of its limited solubility, succinic acid was used for two main reasons. First, we had previously characterized aqueous solutions of succinic acid with our vapor pressure apparatus. This meant we had previous vapor pressure data for the pure aqueous compound at different concentrations and temperatures. Second, we wanted to compare our results to a previous study on mixtures done by Svenningsson et al. (2006) which used the HTDMA. They employed succinic acid in all their mixtures as representative of the dicarboxylic acids category (II) of organic matter. Using identical mixtures except for the fulvic acid allowed us to compare different fulvic acids as analogs for HULIS.

In the future, we would like to explore solutions with malonic and glutaric acid as representative of category II of organic matter in multicomponent solutions.

3. Can you remake figure 2 with water activity on the y-axis rather than water vapour pressure, its quite hard to follow any trends with temperature as they are masked by the Clausius-Clayperon relation (VP increasing exponentially with temp)

Figure 2 has been re-created as suggested by the reviewer and replaced in the manuscript.

4. When comparing these bulk results with those from particle based measurements (HTDMA, EDB) are there any corrections which need to be made to make them comparable (is a surface tension needed?).

The reviewer raises a valid concern. The effect of the particle curvature on the vapor pressure, or Kelvin effect, can become significant at smaller diameters thus making it difficult to compare bulk results to particle-based measurements. This is why we stated that our calculations only apply to particles above a certain diameter (page 1053, line 16), where we assumed that the Kelvin correction was below 5%.

In our next study, we measured the surface tension of a subset of the solutions presented in the current study in order to assess the magnitude of the Kelvin effect on the water activity of sub-micron particles composed of pure and mixed WSOC solutions. We found that the minimum particle diameter assumed ($0.05\ \mu\text{m}$) for the pure solutes was too low, and that a more appropriate diameter above which the Kelvin effect is negligible (or at least within our uncertainty range) is $0.10\ \mu\text{m}$. For the humic substances and their mixtures, the diameter assumed was appropriate.

These results constitute Chapter 4 of the doctoral thesis of Zamora et al., 2013 (see complete reference at the end) and will be submitted for publication soon.

In accordance with our results obtained after the submittal of this manuscript, the text has been slightly modified as follows (changes/next text in blue):

“Because the Kelvin effect was not considered in this study, the calculations in this section apply to particles $> 0.10\ \mu\text{m}$ in diameter for the inorganic salts, levoglucosan and succinic acid, and for particles $> 0.20\ \mu\text{m}$ in diameter for the humic substances and their mixtures. Our measured surface tension data show a Kelvin correction smaller than the associated uncertainty of water activity above these diameter values.”

5. With the multicomponent mixtures you state that interactions may explain the differences in hygroscopic growth. Have you tried modeling this? AIOMFAC (<http://www.aiomfac.caltech.edu/>) and E-AIM (<http://www.aim.env.uea.ac.uk/aim/aim.php>) have tools for modeling solute and solvent activities. I strongly suggest you at least look at these tools as they could provide a lot of insight into what is happening in the multicomponent mixtures. You may need to use some of the assumptions about humic substances Svenningsson has made (pg 1059 ln20)

Kindly see answer to question 4 from Reviewer 2, since both questions deal with the same topic.

6. In your conclusions you recommend studies of chamber extract to represent HULIS due to the widely varying hygroscopic behavior depend on the humic substance origin. This would be suitable for HTDMA and EDB but I don't think it would work for bulk studies (such as this one). Could the authors suggest a well defined compound or mixture of compounds that would better represent HULIS for bulk experiments? If not could they perhaps add a short discussion at the end (or even here in the comments) of the necessary properties a bulk HULIS substitute should have.

The reviewer brings up a good point about the chamber extract being especially suitable for study with the HTDMA and EDB instruments rather than a bulk method, presumably referring to the small quantity of SOA residue that can be collected per batch. This issues is also related to

In order to address question 6 and 7, we have modified the text as follows (changes/new text are in blue):

"We have also demonstrated that the ZSR approach works reasonably well for the multicomponent mixtures studied under $a_w = 0.95$, but can produce large deviations at higher values. *Based on our findings*, we recommend that similar studies be performed with *an analog more representative of HULIS in place of humic substances. One option could be to use chamber generated secondary organic aerosols (SOA)*, in order to better represent the influence of HULIS in the hygroscopic growth of atmospheric particles. *However, we recognize this approach may not yet be suitable for bulk studies. It is likely that the quantity of SOA residue required to prepare the bulk solutions needed would exceed the amount that could be generated in a smog chamber. Although it may be possible to design a process to collect enough SOA from multiple chamber runs, reproducibility would be a concern. Another option would be to find a substitute chemical for HULIS. A bulk HULIS analog should ideally have uniform properties from batch to batch, a known molecular weight, and similar surface activity and aromatic moiety content to HULIS. While the search for a better HULIS representative is ongoing, additional studies with humic substances can still provide insight into the behavior or multicomponent mixtures in atmospheric aerosols.*

7. Would you suggest we abandon humic and fulvic acids or do you think they still have a role to play as proxies for HULIS.

Kindly see answer to question 6 from Reviewer 1.

Reviewer 2

In this paper the authors present a study on the water activity of mixed systems comprised of humid like substances and various inorganic salts. The study presents some interesting results with regards to the breakdown of additivity assumptions at high concentrations. I recommend

publication after the following comments are addressed.

General comments:

1. What are the reported accuracies for water activity measurements using bulk methods and how do they compare with levitation techniques?

Good question. We have added the following to the manuscript text to answer question 1 and 7, since both questions deal with the same topic:

“In the literature, water activity measurements have been reported to have accuracies of $\pm 0.003 - 0.5$ (or $\pm 0.3 - 5\%$ in terms of RH) though most recent studies are in the $\pm 0.3 - 3\%$ range [Zhang et al., 1993a, b; Peng et al., 2001a; Wise et al., 2003; Marcolli et al., 2004]. The uncertainty range for the relative humidity in our study was within this range ($\pm 0.5\%$ at 25°C). Reported measurement uncertainties associated with the electrodynamic balance (EDB) typically range from $\pm 1 - 5\%$ [Cruz and Pandis, 2000; Peng et al., 2001a; Chan et al., 2005] while those associated with the HTDMA approximately vary from $\pm 0.3 - 5\%$ [Cruz and Pandis, 2000; Gysel et al., 2002; Brooks et al., 2004; Dinar et al., 2007]. Bulk methods seem to have similar associated uncertainty to the particle-based methods but have the ability to study higher relative humidities.”

2. Do the authors have any feel for whether any kinetic limitations to mass transfer of water might affect their results? It has been postulated that mixtures of organics may form viscous solutions and thus introduce a kinetic barrier for mass transfer.

The effect of kinetic limitation to mass transfer is definitely a concern when studying the hygroscopic behavior of atmospheric particles, especially large organic polymers such as humic substances. It is clear, though, that this concern is more pronounced for particle-based methods with small solution equilibrium times. Chan and Chan (2005) eloquently described their investigation of mass transfer effects due to low residence time on HTDMA measurements. In their study, they stated that HTDMA data could be assessed against water activity measurements of bulk solutions perhaps suggesting that bulk measurements may be unaffected by mass transfer effects. While we believe it is less of a concern for bulk studies, we have taken steps to minimize these effects as much as possible. We allowed all solutions to equilibrate at the target temperature for 30 minutes. The vapor pressure was only recorded when it had remained unchanged for this entire period. In addition, the solutions were lightly stirred during the entire process. Still, slowed mass transfer due to solution effects remains a possibility and it bears further study.

3. Page 1050. Given the wide uptake of Kappa Kohler theory this should at least be briefly mentioned/discussed. Would it be possible to provide an estimate of the associated Kappa values for these mixtures and how would that compare with measured atmospheric behaviour?

As we mentioned in our answer to question 4 of Reviewer 1, we conducted an additional study where we measured bulk surface tension of pure aqueous solutes and of a subset of the mixtures presented in the current study. Among other objectives, this

work aimed to use water activity and surface tension data to generate Köhler and kappa-Köhler activation curves, and compare predicted critical supersaturation curves for the mixtures studied with measured CCN data for HULIS samples. Table 4.2 lists the kappa values obtained for all the pure solutes and NAFA mixtures presented in this study, except for Fluka humic acid. These results constitute Chapter 4 of the doctoral thesis of Zamora et al., 2013 (see complete reference at the end) and will be submitted for publication soon.

While the kappa-Köhler subject is very much relevant to the current study, we feel that we can discuss it and include it more thoroughly in this study.

4. Following the first referee i think it would be highly useful for the community to see how well available mixed inorganic-organic activity models compare with your results. Whilst i understand the difficulty in prescribing functionality to humid like material, it would be at least useful to discuss why this isn't possible.

We completely agree that comparing our results to other available mixed inorganic-organic activity models such as AIOMFAC and E-AIM could provide insight into our findings. However, as Reviewer 2 states, many assumptions would need to be made to run these models (such as molar mass, molar volume, and solubility), which could greatly impact the outcome. For NAFA, molar mass estimates can vary from 510 – 4410 kg/kmol and no estimates are available for Fluka humic acid. One of the main advantages of the ZSR method we used is that mass-based water parameterizations could be used thus avoiding the need for molar mass assumptions. In addition, all the systems would have to be studied with these models in order to assess the results thoroughly. We feel that this endeavor would be best treated as a separate project.

5. The authors report a Vant Hoff factor of 0.28 for the mixture 'NRFA-MIXORG'. As the Vant Hoff factor is used to describe dissociation levels, can the authors describe what effect this might be down to aside from the assumptions of molecular weight?

The following has been added to the manuscript text in the same section (changes/next text in blue):

"The van't Hoff factors obtained for NAFA-MIXORG and HA-MIXORG were 0.28 and 1.10, respectively (Fig. 4). Assuming our molar weight estimates for the humic substances are accurate, these values indicate that HA-MIXORG behaved almost ideally while NAFA-MIXORG *appeared to deviate* substantially from ideality. *It is worth noting that due to solubility issues with succinic acid, the factor for NAFA-MIXORG incorporates considerably less data points than all other solutions presented and therefore is a not reliable indication of ideality or dissociation levels.*"

Specific questions:

6. Page 1052 Section 2.3 - 'The uncertainty associated with the water activity at 25°C of pure solutes was reported to be between 0.007 and 0.018 in our previous work'.

Over what RH range was this found over?

The following sentence has been added to the manuscript text in the same section:

“This uncertainty range was found over a relative humidity range of 70 – 99.9%.”

7. How does the reported error in RH compare with other methods such as the EDB?

Kindly see answer to question 1 from Reviewer 2, since the question deals with a related subject.

References

Zamora, I. R., Jacobson, M. Z., Golden D. M., and Hildemann, L. M.: Characterizing the Physicochemical Properties of Organic Matter In Atmospheric Aerosols: Effects of Humic-Like Substances On Hygroscopic Growth and Cloud Activation. Thesis (Ph.D.)-Stanford University, 2013. Link:
<http://searchworks.stanford.edu/view/9957603>