Response to reviewer comments
Manuscript acp-2014-912: Influence of particle phase state on the hygroscopic behavior of mixed organic-inorganic aerosols

Anonymous Referee #1

General comments:

The phase behavior, the hygroscopicity, and viscosity of atmospheric aerosols are important to understand the processes in the atmosphere. More studies on these properties of aerosols have been conducted in the recent few years. However, current studies are still limited. This manuscript investigated the phase behavior and hygroscopicity of selected mixed organic-ammonium sulfate aerosols by measuring the water uptake growth. They also used models to predict the water uptake growth for these mixed systems. This study adds to the understanding of hygroscopicity and phase behavior of particles, especially for the submicron size range. This paper is well written, and results are clearly presented. I have a few minor comments the authors should consider before the final publication.

Specific comments:

In the section 3.1.1, the authors discussed possible reasons why AIOMFAC model predicted RH values at which two-phases merge into one phase are higher than the RH values reported in You et al. (2013). I agree with these two possible reasons. And I am curious if there is any hysteresis in these phase separation-phase merging processes in these two investigated systems. In the You et al. all the results were from experiments when RH decreased from high to low values. In AIOMFAC prediction in this study, RH increased from low to high values. It may be useful to think about it using the phase diagrams, such as phase diagrams in Song et al. (2012a). I think the hysteresis may depend on different mixed organic-inorganic salt systems.

We have added a discussion regarding potential hysteresis of the RH at which separation and merging of phases occurs for the diethylmalonic-ammonium sulfate and 2-methylgluratic–ammonium sulfate aerosol systems and discuss this directly in terms of the potential influence on disagreement between previous experimental results and AIOMFAC-predicted phase transitions.

Revisions in text:

In regards to the diethymalonic acid-ammonium sulfate system:

“In addition, You et al. (2013) performed dehydration experiments to explore the onset of phase separation (from high to low RH), while the present study focused on hydration experiments (from low to high RH). AIOMFAC predictions are made under the assumption that there is no hysteresis between LLPS and the merging of two liquid

phases to a single phase in terms of the onset RH. This is because experiments (e.g., Song et al., 2012a) show that there is little to no hysteresis in such a phase transition, at least for systems with liquid-like viscosities. In contrast to the typical hysteresis behavior of liquid-solid/solid-liquid phase transitions (i.e., deliquescence vs. crystallization), liquid-liquid to single-liquid phase transitions involve only disordered phase states (rather than crystalline solids with long-range order). Exceptions to this may exist for some systems in a particular composition range involving the metastable region of a liquid-liquid equilibrium phase diagram (e.g. Zuend et al., 2010). However, the energy barrier for the nucleation and growth of a new liquid phase is small in comparison to the larger energy barrier that needs to be overcome when a new crystalline phase is formed. Because the merging of the phases is predicted to occur at an RH at which aqueous diethylmalonic acid is expected to be of low viscosity (Figure 1a), no hysteresis behavior is expected. Thus, we do not expect that a hysteresis behavior influenced the disagreement in the RH of phase merging discussed above."

In regards to the 2-methylglutartic acid-ammonium sulfate system:

"Again, as is explained above, no hysteresis is expected for the phase separation and merging for hydration and dehydration conditions for this system."

Page 32939, line 26: I suggest you could add the following two papers as references to here, because these two studies investigated samples from ambient environment and could support your statement here. Y. You, L. Renbaum-Wolff, M. Carreras-Sospedra, S.J. Hanna, N. Hiranuma, S. Kamal, M.L. Smith, X.L. Zhang, R.J. Weber, J.E. Shilling, D. Dabdub, S.T. Martin, and A.K. Bertram, P. Natl. Acad. Sci. USA 109, 13188 (2012). C. Pöhlker, K.T. Wiedemann, B. Sinha, M. Shiraiwa, S.S. Gunthe, M. Smith, H. Su, P. Artaxo, Q. Chen, Y.F. Cheng, W. Elbert, M.K. Gilles, A.L.D. Kilcoyne, R.C. Moffet, M. Weigand, S.T. Martin, U. Pöschl, and M.O. Andreae, Science 337, 1075 (2012).

We thank the reviewer for bringing these publications to our attention and have added them as suggested.

Page 32948, line 16. in Bertram et al 2011, particles containing citric acid mixed with ammonium sulfate were also studied and no LLPS was observed, so you may also want to add it to here as a reference.

We have added this reference to the text, as suggested, and to table 1.

Page 32952, second paragraph: the results in Figure 3c, the measurements, and dashed line (AIOMAC+dehydration), are also consistent with recent experiemental re- sults in You and Bertram (2014). LLPS was not observed in particles containing su- crose mixed with ammonium sulfate (mass ratio = 2:1). Y. You and A. K. Bertram. Effects of molecular weight and temperature on liquid–liquid phase

separation in parti- cles containing organic species and ammonium sulfate. Atmos. Chem. Phys. Discuss., 14, 23341-23373, 2014

The final, revised version of the recommended paper is now considered in our discussion of the AIOMFAC-predicted phase behavior of the sucrose-ammonium sulfate system with an organic:inorganic ratio of 2:1:

"The predicted occurrence of LLPS for sucrose (O:C = 0.92) contrasts with previous studies that suggest that LLPS is unlikely for organic compounds with O:C > 0.7 – 0.8 (Bertram et al., 2011; Song et al., 2012b; You et al., 2013), as well as the experimental results of You and Bertram (2015), in which no LLPS was observed for sucrose-ammonium sulfate particles with an organic to inorganic mass ratio of 2:1."

Table 1, for the last row, You and Bertram (2014) (mentioned above) also studied the LLPS of particles containing sucrose mixed with ammonium sulfate, dry mass ratio 2:1, and no LLPS was observed, so you may want to add this to here as well.

Table 1 has been updated to include this reference as suggested. We also now note this reference in our discussion of previous characterizations of the phase behavior of the systems studied here:

"*The phase behavior of these systems as a function of RH, however, has only been characterized for a sucrose:ammonium sulfate dry mass ratio of 2:1 (You and Bertram, 2015, Table1).*"

Technical corrections:

Page 32943 line 5: microscope is more accurate than telescope

This typo has been corrected.

Page 32943, line 22: Could you please write out the glass transition temperature of sucrose here, so readers can directly know it when reading.

We have added the following text:

"Sucrose was selected as a model compound in that work due to its high glass-transition temperature (T_g = 335.7K), as characterized by Zobrist et al., (2008)"

Page 32954 line 5: it should be You et al. 2013, not 2012 Table 1, for the first three rows, the reference should be You et al. 2013, not 2012

These corrections have been made.

Anonymous Referee #2

Review of the paper: "Influence of particle phase state on the hygroscopic behavior of mixed organic–inorganic aerosols", by Hodas et al.

General comment: This nicely written paper presents indirect measurement of particle phase state for different mixed organic-inorganic aerosols at different relative humidities. This paper explores the extent to which phase separations and other complex phase behavior influence the partitioning of water to particle phase. The reported data have been measured with a DASH-SP, and the data are compared with theoretical values obtained by several models (from complex model such as AIOMFAC to very simple model). The discrepancies and agreements among the different RH and models are discussed. This paper contributes to a better understanding on the hygroscopic behavior of mixture of organic-inorganic for both experimentalists and modelers. For experimentalist as for example, it underlines the effect of drying on the properties of aerosol, which could explain for example why instruments such as HTDMA are able to measure in a consistent way the hygroscopicity of inorganic aerosol, but still have difficulties to measure secondary organic aerosol hygroscopicities (see the different HTDMA intercomparison papers). And for modeler as it discusses the limitation of different simple modeling approaches usually used in global modeling. I recommend the publication of this paper.

Minor comments:

-O:C ratio is used in this paper (as in other papers) to provide a hint of the hygroscopicity of the aerosol. However, recent studies have shown that average carbon oxidation state, OSc, may be a better indicator of aerosol oxidation than O:C as O:C may not capture oxidative changes due to the breaking and forming of bonds (Kroll et al., 2009 and 2011). This could be mention, although, it is not the scope of this paper.

We agree that parameterizations of hygroscpoicity based on $\overline{\mathrm{OS}}_\mathrm{C}$ should also be a consideration in future work and may be valuable to future efforts to model water uptake by complex organic and mixed organic-inorganic aerosol systems. O:C is a relatively versatile approximate measure of the polarity of organic compounds or the average in a mixture of organic compounds, particularly when the system components are known, as in the case of our model systems. The mean carbon oxidation state may be a useful measure when, in addition to a known initial composition, the goal is to track the progression of oxidation and fragmentation of organic molecules in an atmospheric chemistry model. We now touch on this in the discussion:

"*Parameterizations of LLPS and other complex phase behavior based on commonly measured variables such as O:C…may prove valuable in applying the simplified HGF calculation approaches explored here in large-scale models.* ***Average carbon oxidation state ($\overline{OS}_C$) has also been presented as an indicator of the degree of aerosol oxidation (Kroll et al., 2011) and may be a useful measure when the goal is to track changes in hygroscopicity with the progression of oxidation and fragmentation of organic***

molecules in an atmospheric chemistry model. Parameterizations of hygroscopicity based on $\overline{OS}_C$ might also lead to advancements in the modeling of aerosol water uptake for complex organic and mixed organic-inorganic systems and should be a consideration in future work."

-The possible effect of fast drying is well discussed in the paper, however the effect of short residence time at the studied RH (only 4 seconds) is not too much discussed. How does the residence time at the measured RH could influence the presence of 1 or 2 liquid phases?

We have added a discussion regarding the potential influence of the short residence time on the phase behavior of the aerosol systems to the Measurement and Modeling Limitations and Uncertainty section:

"Finally, the timescale of humidification in our experiments differs from that in the single-particle studies. For example, in the mixed dicarboxylic acid-ammonium sulfate single-particle experiments, RH was changed at a rate of 0.14 – 0.34% min^{-1} (Song et al., 2012). The extent to which the timescale of humidification influences of the occurrence of phase separation is unknown; however, again, agreement between the measured hygroscopic growth and those calculated under equilibrium conditions suggests humidification timescale did not have a substantial impact on phase behavior."

-in 2.1 Methods: The authors have used DASH-SP for this study. Is there a particular advantage compare to use a HTDMA?

The DASH-SP was designed to address the time-resolution limitations of the HTDMA and is specifically geared towards use in airborne field campaigns. A field campaign in which hygroscopic behavior of ambient aerosols will be measured is planned for the coming summer and the present study will serve as a basis for that work; however, we do not feel that this is relevant to the presentation of the methodology/results in the present study and as a result, we do not discuss the specific details of an HTDMA-DASH comparison.

-P32947: . . . (with no water uptake on the timescale of the experiment). There the 4 seconds could be repeated as it is a very short time.

We have modified this statement as follows:

"*with no water uptake on the timescale of the 4 s residence time in the humidifier*"

- In Section 3.2: The 3 different conditions described should have for reading simplicity the same name in figure 4. (Easier to go from text to figure).

This is a good suggestion and we have edited the text as follows to ensure ease of going between the text and Figure 4:

"…we compared the rigorous thermodynamic modeling of the AIOMFAC-based equilibrium HGF predictions ***("AIOMFAC, equilibrium" in Figure 4****) to that based on several simplified thermodynamic assumptions: (1) representing particles as ideal, well-mixed liquids* ***("Ideal – well-mixed liquid")****, (2) forcing a single liquid phase following the deliquescence of ammonium sulfate, but accounting for non-ideal interactions through activity coefficient calculations and allowing for a SLE of ammonium sulfate* ***("No LLPS – non-deal"),*** *and (3) a ZSR-like calculation in which complete separation between the inorganic and organic components is assumed at all RH levels* ***("Complete Phase Separation (ZSR))"****... Note that for the diethylmalonic acid-ammonium sulfate system, we first focus on the calculation for which the presence of a solid organic is predicted prior to particle deliquescence* ***("Solid Organic" in Figure 4)****.*

-Table 1: The different organic densities used for the model could be added to table1.

Table 1 has been edited to include organic-component density as suggested.