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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Hygroscopic and phase separation properties of ammonium sulfate/organic/water ternary solutions" *by* M. A. Zawadowicz et al.

Anonymous Referee #1

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This manuscript discusses hygroscopic properties and related phase transitions of atmospherically relevant aerosol particles using FTIR spectroscopy coupled to a flow tube. In addition, the authors show interesting and new approaches of the phase transition regarding the D2O vapor as a function of RH. The physicochemical properties of aerosol particles have become an area of intense scientific interest. Providing new measurements and evaluations, the current manuscript is suitable for Atmospheric Chemistry and Physics. However, given that result of the phase transitions in aerosol particles such as deliquescence, efflorescence, and liquid-liquid phase separation have been reported in many recent studies, additional scientific findings provided

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in the present manuscript are somehow limited. Therefore I suggest the authors to provide more experimental data to validate their new approach with existing studies in the literature. Furthermore, more convincing statements of the advantage of the current work supported by additional experimental results should be included in the manuscript. I would recommend its publication after addressing the general and specific comments below.

General comments:

The authors mention the size effect on phase separation in the investigated systems based on the results of Veghte et al. (2013). However, the chemical compositions of the model systems (polyols) in this study are different from those of Veghte et al. (2013) (acids). At present time, there is no evidence of size effect on phase separation in aerosol particles consisting of polyols and ammonium sulfate so the current model system results should not directly be compared to other studies to draw a conclusion on the size effect on phase separation. Therefore, the authors should provide more experimental data to make clearer statements of the size effect on phase separation of polyol/ammonium sulfate particles. As a first step, I would suggest the authors to validate the size effect by using the same model systems of acids/ammonium sulfate that Veghte et al. (2013) used. In addition, the authors could specify the particle size range for the occurrence of phase separation in the manuscript. Temperature during the experiments needs to be stated. It should be mentioned how the temperature was controlled during the spectroscopic experiments.

Specific comments:

1. Abstract: The abstract focuses too much on introducing the topic (half of the abstract). Please describe more what the new findings and the summary of the presented work are.

2. Introduction:

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- The structure of the introduction is at some point hard to follow. For example, the authors describe literature work and suddenly introduce the model systems of this study in page 6542, line 12-13 and page 6541 line 4-5. I would suggest the authors to make a paragraph in the end of the introduction to introduce the model systems, motivation, objectives, and outline of this study.

- 6542, line 2-5: Please rewrite this sentence. Phase separated particles can show core-shell morphology or partially engulfed morphology (Kwamena et al., 2010; Reid et al., 2011; Krieger et al., 2012; Song et al., 2013). In addition, even though liquid-liquid phase separation occurs in a mixed particle, some fractions of organic can be found in inorganic phase (Krieger et al., 2012; Ciobanu et al., 2009; Song et al, 2012; You et al., 2014).

- 6542, line 14-22: This paragraph describes the mechanism of liquid-liquid phase separation. However, it seems that this is unnecessary because the current work does not show any processes or mechanisms of liquid-liquid phase separation.

- Citations:

- 6540, line 10-18: Please distinguish the references properly by clearly separating those discussing phase transition of single particle and those discussing phase transition of particles on a substrate.

- 6541, line 18-22: Please check the references. Not all references discussed malonic acid. In addition, do the authors refer to Ciobanu et al. “2010” for the nucleation of ammonium sulfate?

- 6542, line 25: Are all references showing the evidence for liquid-liquid phase separation using microscopy and EDB? Please cite only references where liquid-liquid phase separation was observed

3. Experimental:

- 6543, line 16-18: It would be useful to mention the investigated ratios of ammonium

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sulfate and organics.

- 6544, line 11: What type of salts have the authors used for the humidity calibration?

- 6545, Fig. 3: It is difficult to follow the sentences together with the figure. Please add shaded areas in the figure to discriminate the different bands.

- 6546, line 7-9: Please add references for the signatures.

4. Results and discussion:

- 6547, Fig. 5: The DRH of ammonium sulfate seems to be between 75-80 %, which is the DRH range that the authors should state in the manuscript (not 80%). In addition, it is difficult to capture the DRH from Figure 5 (eg. 1,4-butanediol/ammonium sulfate for 1:1). Marcolli and Krieger (2006) showed the DRH ∼80 % in the mixture of 1,4-butanediol/ammonium sulfate. Please compare and discuss this result with literature results.

- 6547, line 8-13: The authors observed DRH of ∼40 % for 1:3 glycerol/ammonium sulfate solution. However, literature studies showed that mixed glycerol/ammonium sulfate particles of similar organic/inorganic ratio have a higher DRH. Do the authors have explanations of the discrepancy?

- 6548, line 18-22: In many other places, the authors mention size effect on phase transitions of aerosol particles. The specific size range from which the authors can discriminate small and large particles from their measurements in comparison to those of Veghte et al. (2013) should be stated.

- Section 3.2: It would be useful for readability of the manuscript to compile a table of the result summary discussed in the text (SRH, ERH, DRH and gas-phase exchange).

5. Conclusions:

6551, line 10: which theory are the authors referring to?

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6. Table 2:

- Please add all results with different organic to ammonium sulfate ratio investigated in this study and available in the literature. It should be given what N/A stands for.

7. Figure 5 and 6: Please modify the legend (eg. hydration and dehydration) since all the data points do not indicate deliquescence and efflorescence. The authors could use shaded area to indicate the RH range where those processes take place.

References:

Ciobanu, V. G., Marcolli, C., Krieger, U. K., Zuend, A., and Peter, T.: Efflorescence of Ammonium Sulfate and Coated Ammonium Sulfate Particles: Evidence for Surface Nucleation, J Phys Chem A, 114, 9486-9495, Doi 10.1021/Jp103541w, 2010.

Krieger, U. K., Marcolli, C., and Reid, J. P.: Exploring the complexity of aerosol particle properties and processes using single particle techniques, Chem Soc Rev, 41, 6631-6662, Doi 10.1039/C2cs35082c, 2012.

Kwamena, N. O. A., Buajarern, J., and Reid, J. P.: Equilibrium Morphology of Mixed Organic/Inorganic/Aqueous Aerosol Droplets: Investigating the Effect of Relative Humidity and Surfactants, J Phys Chem A, 114, 5787-5795, Doi 10.1021/Jp1003648, 2010.

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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 sep-

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Zardini, A. A., Sjogren, S., Marcolli, C., Krieger, U. K., Gysel, M., Weingartner, E., Baltensperger, U., and Peter, T.: A combined particle trap/HTDMA hygroscopicity study of mixed inorganic/organic aerosol particles, Atmos Chem Phys, 8, 5589-5601, 2008.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 6537, 2015.