

Interactive comment on “Phase transitions and hygroscopic growth of aerosol particles containing humic acid and mixtures of humic acid and ammonium sulphate” by C. L. Badger et al.

Anonymous Referee #1

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This is an interesting study that employs FTIR spectroscopy and TDMA to investigate the hygroscopicity and composition of aerosol particles containing humic acid (HA) and mixtures of HA and ammonium sulphate. Humic like substances are an important but poorly understood group of water-soluble organic compounds in atmospheric aerosols. By analyzing the FTIR spectra and the TDMA data, the authors clearly show that aerosol particles containing HA can exist as solution droplets at low RH (RH <2%) and there is a complex interaction between the HA and ammonium sulfate, which can alter the phase transition of ammonium sulfate. The paper is well written and is a good addition to the literature in the phase transformation and hygroscopic

properties of atmospheric aerosols. I recommend publishing the paper after clarifying some minor points below.

Specific comments:

Experiments - What are the typical particle concentrations used in these experiments?

Page 9585, line 18 - The pH of solutions containing LSHA was adjusted to $\text{pH} = 7$ with the addition of NaOH to simulate atmospheric aerosol acidities more closely and to allow most of the LSHA to dissolve. In the NaHA experiment, the pH of NaHA solutions was adjusted to two pH values ($\text{pH} = 4$ and 9) to study the effect of pH on the hygroscopicity of aerosol particles. Is there any reason why the two HA solutions were adjusted to different pH? Furthermore, different chemicals were used to adjust the pH of the HA solutions to various desired values. Any idea of the effects of the added solutions on the hygroscopic measurements? For example, Figure 6 shows that the data of pH9 NaHA and pH4 NaHA solutions appear to diverge at RH larger than 70%, although they may also be within the experimental uncertainty. I am not very clear on how the measurements of solutions prepared at different pH should be interpreted and compared. Is it true that pH of the solution does not play any role at all?

Page 9590, line 15 (and Figure 4) - Is the increasing extinction at wavenumbers higher than 3500 cm^{-1} due to Mie scattering? It would be useful if the authors described how the water peaks are distinguished from the general upward trends of absorption at higher wavenumbers.

Page 9590, line 24 - The use of the $1000\text{-}1400 \text{ cm}^{-1}$ as an “internal standard” is understandable. However, it should be cautioned that when one compares the water peak data of particles of different HA, such “internal standard” may not be universal across all the samples.

Page 9592, the shifts of the NH_4^+ peak during deliquescence were discussed. The authors attributed these shifts to the complex formation of ammonium with humic acid

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(and with malonic acid in their previous work) and the partial crystallization of AS. The results are very interesting. The 1.5:1 NaHA:AS mixture has the NH_4^+ peak at about 1440 cm^{-1} at very small RH ($<2\%$). It is not likely that the small amount of water present at such low RH can lead to a significant portion of aqueous AS (without being influenced by interaction with HA) that result in the peak at 1440 cm^{-1} . Besides, the authors also found that Equation (1), which assumes no interaction between AS and HA, predict the measured hygroscopic growth well. Presumably, AS is assumed dry at such low RH. Overall, I feel that the amount of water present at low RH may be too small. Any water present may be associated with the HA than with AS and hence the interaction effect between HA and NH_4^+ may be the dominant reason for the peak shifts.

Page 9593, line 10 and more - The authors explained the dip in the absorption band of NH_4^+ prior to deliquescence by the formation of more AS solid due to the presence of water, mobilizing more uncrystallized AS and facilitating their crystallization. Can this explain the larger shift of the 1.5:1 mixture shown in Figure 8A?

Page 9593, line 24 - The water content curves reveal two phase changes (at 65% RH and 76% RH) for the 1:13 NaHA:AS aerosol particles during a deliquescence mode experiment, shown by the red line in Fig. 8A. The authors attributed the first phase change to the deliquescence of HA or sodium sulfate. The second phase change was attributed to the deliquescence of the ammonium sulphate. Did the authors observe similar phase change phenomena in other mixtures with different NaHA:AS mass ratio? Or the authors did mean so when they said the results are “reproducible over several experiments”. What are the contents of sodium in the NaHA and LSHA?

Page 9595, top - The authors state that the phase transitions of aerosol particles containing NaHA and the mixture of NaHA and ammonium sulfate were consistent with the FTIR measurements. It should be noted that the composition of aerosol particles investigated in TDMA measurements are slightly different from that in the FTIR measurements.

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Page 9598, line 4 -10: The authors compared their results with EDB measurements by Chan and Chan (2003) and commented on the possibility of mass transfer limitation in their measurements. They also stated that “our measurements are in general agreement with others showing that efflorescence does not occur readily with these species.” It is interesting to note that the cited measurements made by “others” shown in Table 5 were all based on TDMA too.

Chan and Chan (2005) recently argued that it is possible to have mass transfer complications in hygroscopic measurements using TDMA or aerosol flow tube systems when studying organic containing aerosols. They further proposed that experimentation of hygroscopic measurements with different residence times would be useful to confirm equilibrium measurements. Along this line of thinking, results at different residence time of the current study, if available, would be useful in this paper.

Page 9601: Cloud processing can also be a possible mechanism for HULIS formation (Hoffer et al.)

Figure 7: It would probably be more interesting to show the spectra in relative scale so that all peaks can be compared with the same intensity of a reference peak, e.g. sulfate. This can perhaps highlight the differences of the spectra better.

References Chan, M. N., Chan, C. K. (2005) “Mass Transfer Effects in the Hygroscopic Measurement of Aerosol Particles”, *Atmos. Chem. Phys.*, 5, 2703-2712.

Hoffer, A., Kiss, G., Blazso, M., Gelencser, A. (2004) “Chemical characterization of humic like substances (HULIS) formed from a lignin-type precursor in model cloud water”, *Geophys. Res. Lett.*, 37, L06115, doi:10.1029/2003GL018962.

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