

## ***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.***

**C. L. Badger et al.**

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### **Response to Referee #1**

The authors thank the referee for his/her constructive comments and have amended the manuscript accordingly. Specific points are addressed below.

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

This information has been added to the revised manuscript.

*Page 9585, line 18 - The pH of solutions containing LSHA was adjusted to pH = 7 with the addition of NaOH to simulate atmospheric aerosol acidities more closely and*

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*to allow most of the LSHA to dissolve. In the NaHA experiment, the pH of NaHA solutions was adjusted to two pH values (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?*

The pH values were chosen largely from a practical perspective, especially in the case of the Leonardite HA which was not found to dissolve sufficiently in distilled water. The pH of the Aldrich humic acid was adjusted to investigate whether the presence of the carboxylate anion (as opposed to protonated carboxylic acid groups) affected the water content and phase transitions of the humic acid aerosol. As the water content curves for the pH 4 and pH 9 NaHA are similar, there is some validity to using an intermediate pH (pH 7) for the Leonardite HA.

*Page 9590, line 15 (and Figure 4) - Is the increasing extinction at wavenumbers higher than  $3500\text{ cm}^{-1}$  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.*

Yes, this increase is due to Mie scattering and the areas of the water peaks were calculated taking this underlying increase into account. The manuscript has been amended to reflect this.

*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*

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across all the samples.

This has been noted in the revised manuscript.

*Page 9592, the shifts of the  $\text{NH}_4^+$  peak during deliquescence were discussed. The authors attributed these shifts to the complex formation of ammonium with humic acid (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  $\text{NH}_4^+$  peak at about  $1440\text{ cm}^{-1}$  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  $1440\text{ cm}^{-1}$ . 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  $\text{NH}_4^+$  may be the dominant reason for the peak shifts.*

Whilst we are uncertain as to the mechanism driving the peak shift, we do agree that low water content at low RH does lend some weight to the complex formation argument and merits further study. The manuscript has been amended to reflect this.

*Page 9593, line 10 and more - The authors explained the dip in the absorption band of  $\text{NH}_4^+$  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?*

This larger shift can be explained by either the presence of more humic acid-ammonium complex originally or by the fact that there is more water associated with the particles. The manuscript has been amended to reflect this.

*Page 9593, line 24 - The water content curves reveal two phase changes (at 65% RH*

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*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?*

Two phase changes were seen in all studies of this particular NaHA:AS ratio aerosol, the 1:13 NaHA:AS. Only one phase change was seen for the 1.5:1 and 1:1 aerosols. This paragraph has been amended in the revised manuscript. It is felt that the two phase changes are a result of some chemical difference in the 1:13 NaHA:AS aerosols compared with the other aerosols, not that a potential second phase change in the 1.5:1 and 1:1 NaHA:AS aerosols is masked due to instrumental detection limits. In principle the quantity of Na in the solutions could be analysed but these experiments were not carried out. It is not possible to calculate this on a stoichiometric basis as the rfm of the humic acid is not known or indeed is the number of carboxylic acid groups per molecule.

*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.*

This has been noted in the revised manuscript.

*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.'*

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*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.*

This is an important point but no experiments were done for different residence times as the current experimental set-ups do not allow for this. See also our response to the comments from Referee #2.

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

This has been added to the revised manuscript.

*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.*

This is a good suggestion and the figure has been amended.

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Interactive comment on Atmos. Chem. Phys. Discuss., 5, 9581, 2005.

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