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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Hygroscopic growth and activation of HULIS particles: experimental data and a new iterative parameterization scheme for complex aerosol particles" *by* M. Ziese et al.

M. Ziese et al.

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Thanks to the referee for the review. Below, we repeat your comments and then give our responses and explanations on what we did to meet your suggestions and requirements.

Comments

—– review: p 13775, l. 9-29: This part needs better organization: If HULIS comprise 60% of total organics, the fraction in WSOC should be higher. A growth factor of 1.08 points to HULIS that is rather insoluble and, thus, is not a fraction of WSOC. Can the differences in surface tension be related to the age/source of HULIS? It would be useful here to introduce terms like 'aged HULIS' and 'fresh HULIS' as this concept will

be useful later in the manuscript in order to explain the differences in the presented results to prior studies.

our comment: This section, together with the two following ones, has been reorganized, and the concept of fresh and aged HULIS is now introduced. However, we continue to consider HULIS as a soluble substance. Was it not soluble, it wouldn't have the effect on the activation that we (and others before us) observed, Also, the extracts of HULIS readily dissolve in water in the lab (e.g. for our particle generation).

—– review p. 13776, l. 12: The promise that a consistent parameterization for HULIS will be presented is a bit bold. Make clear that it only refers to the HULIS samples analyzed in the present study (but also see my comments below).

our comment: We rewrote this part, making clear now that the parameterization could be fit to our two HULIS samples. We also added, following one of your comments below, an analysis of data from Dinar 2006 and Dinar 2007 (which worked out well, too), and mention this here, now, too.

—– review: p 13777, l. 4/5: What is the time the particles spend in the tube? How do you make sure that they reach equilibrium diameter?

our comment: The residence time of the particles in the LACIS flow tube under constant relative humidities below 100% was 2 sec during the experiments. This time is now given in the text. Due to the very limited mass of our HULIS sample, we were unable to do experiments with varying residence times. However, as the HULIS particles activated readily, and as the super-saturation in LACIS is only reached for a fraction of a second, we assume that also the hygroscopic growth has taken place on timescales shorter than the two seconds. This is now said explicitly in the text, too.

—– reveiw p 13777, l. 18: Is the refractive index of HULIS used here based on a similar HULIS sample? How has the refractive index of the mixed sample been derived?

our comment: The refractive index of the HULIS sample was taken from a publication

ACPD

7, S9207–S9212, 2008

by Hoffer et al. 2006, by lack of other data. By now, an additional work on the optical properties was published (Dinar et al. 2008, Faraday Discussions), that describes the complex refractive index of HULIS. Values for the real part of the refractive index in this work range from 1.56 to 1.64, depending on sample and wavelength. The smallest hygroscopic growth factors that we measured with LACIS in this study were 1.7. As described in the manuscript, when determining the sizes of the hydrated particles, a change of the refractive index with increasing size was taken into account by using a volume mixing rule. Therefore, for the smallest measured hygroscopic growth factors, the uncertainties of the refractive index of the hydrated particles are below 1.5%, when values from 1.56 to 1.65 are considered for the pure substances, and these uncertainties will decrease for larger growth factors (i.e., larger RHs). The above now is described in the manuscript, in addition to the example that already had been given for the influence of the uncertainty of the refractive index of the water-extract on the data evaluation. Also, the influence of the neglect of the absorbing part of the aerosol is mentioned there, now, too.

—– review: p. 13778, l. 20 ff: Are there any differences expected between the first and the second HULIS sample? Are there any differences in the total composition between 'spring' and 'summer' samples? Fresh organic are usually less water-soluble than aged ones. How did you make sure that the Aerosol-Water-Extract indeed contained HULIS?

our comment: The actual meteorological and air quality conditions for the first and second aerosol collections were quite similar. More importantly, we only experienced differences in the surface tension properties within the experimental uncertainties between the two sample sets, and hence, the two HULIS sets can be regarded very similar to each other as far as surface tension is concerned. In addition, both sampling campaigns were realized at the same urban site which means similar influence of emission sources. This is now mentioned in the text, at the end of Section 3.2.

The water extraction of the aerosol samples was performed in an identical way for both the water-extract samples and pure HULIS samples. The water extract should,

ACPD

7, S9207–S9212, 2008

therefore, contain the same amount of HULIS for both, the water-extract and the pure HULIS sample. We clarified the text respectively.

—– review: Section 3.2: This section can be shortened. E.g., the first two sentences can be combined; the same could be done with the sentences in l. 18-22. The last sentence of this section is a major finding in this study. I suggest to state the differences in HULIS depending on age/source etc in the abstract of the manuscript.

our comment: We did shorten the indicated passages. Also, we mention the effect of aging/source of the HULIS sample on the coefficients in the parameterization in the abstract, now, citing our results for the data from Dinar 2006 and Dinar 2007.

—– review: p. 13787, l. 15-18: The only variable parameter in rho(ion) is the osmotic coefficient. One reason why it might change with increasing dilution is non-ideal behaviour (as stated here). Another reason could be simply the fact that HULIS contains organic acids that dissociate. Is there any information available on functional groups in the HULIS samples? Repeat here what parameters are included in rho(ion) in order to clarify that compounds with partial solubility exhibit a constant rho(ion) as soluble mass is not included.

our comment: We already hinted towards both in the original version of the manuscript, the possibility of a change in the non-ideality, and a change in the dissociation ('the presence of slightly soluble substances.'). We elaborated this further now, following your suggestion to mention further dissociation. Also we reference equation 4 here, now, the equation that gives the definition of rho(ion). However, we do not have information on the functional groups, so we can not go into any more detail here.

—– review: Section 5.1: It would be useful to apply the procedure in Section 4.2. to other HULIS samples e.g.. based on the studies by Dinar et al., 2007; and Gysel et al., 2005. Comparing these values to those obtained in the present experiments would reflect the range of HULIS parameters for aged vs. fresh HULIS.

ACPD

7, S9207–S9212, 2008

our comment: Gysel et al. (2005) does not give data on activation, so we could not use these data. We did, however, use the data from Dinar 2006 and Dinar 2007. A new paragraph is added to our manuscript (5.3), where the influence of fresh vs. aged HULIS can be seen nicely. Thank you for suggesting to do this!

—– review: p. 13787, l. 19 (Table 2, resp.). What are concentrations [g/l] of HULIS at the point of activation? Are these concentrations realistic for typical atmospheric samples, i.e. when HULIS only comprise a small fraction of the total mass?

our comment: Our calculations yield a concentration of about 30 to 100 g/l of HULIS in water at the point of activation. Necessarily, for each compound that is examined separately, its concentration at the point of activation will be higher than the respective concentration in an internally mixed particle, where additional water soluble substances will contribute to the overall amount of water. This is inherent in every examination of separate compounds. This was one of the reasons for examining the Water-Extract, which, however, only posed new open issues that we, so far, are not able to fully explain.

—– review: Section 5.2: There are previous studies that addressed experimental studies on the hygroscopic properties of humic acid/inorganic mixtures (Badger et al., Atmos. Chem. Phys., 6, 755-768, 2006; Sjogren et al., J. Aerosol Sci. 38, 157-171, 2007). How do these compare to the Aerosol-Water-Extract analyzed here?

our comment: Both of the mentioned studies examined mixtures of 'artificial' HULIS, i.e. 'Aldrich humic acid sodium salt' or an IHSS humic acid. As it is generally discussed, that these substances are different from atmospheric HULIS samples (Graber and Rudich, 2006), the comparability with our study to the two mentioned ones and to similar ones is not straight forward. Also, Badger et al. (2006) examine the influence of an additional inorganic salt on the deliquescence and efflorescence, a topic which we did not examine at all. Sjorgren et al. (2007) find a possible (small) effect of the residence time under humidified conditions on the hygroscopic growth for mixed am-

ACPD

7, S9207–S9212, 2008

monium sulfate/humic acid sodium salt particles. We do mention this now in our study, however, since the effect is really small, it can not explain the fact that our parameterization does not work out for the Aerosol-Water-Extract particles.

—– review: Technical comments (not listed explicitly, here)

our comment: Your technical comments were all followed as you suggested!

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 13773, 2007.

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7, S9207–S9212, 2008

Interactive Comment