

Interactive comment on “Cloud condensation nuclei properties of model and atmospheric HULIS” by E. Dinar et al.

E. Dinar et al.

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We thank the reviewers for providing a thorough and thoughtful reviews. Below please find our reply for each of the comments raised by the reviewers.

Reviewer #1

The paper presents a new study on CCN properties of atmospheric HULIS, presently identified as a major component of aerosol particles in many different areas. The manuscript discusses useful results on the effect of molecular weight and acidity of humic-like substances on cloud activation and uses the Köhler equation to compute dry activation diameters at different supersaturations. The predictions are then compared with measurements performed with a Thermal Gradient Diffusion Cloud Chamber. In

Full Screen / Esc

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particular this paper shows, for the first time in literature, the CCN activity of HULIS extracted from real atmospheric aerosol samples and compares it with the CCN activity of standard SRFA, commonly used as surrogate model compound . There are however some limitations:

1) the use of a constant surface tension (measured at a constant concentration of 1 g/l and thus not dependent on the carbon concentration of the growing droplet)

The reviewers (#1, #2 and #3) are correct that surface activity will be a function of concentration. It is also a function of time. We will show these effects in a future study, as this is a complex issue by itself and will require a separate study. Yet, for the SRFA fractions, our calculation results with the Köhler equation demonstrate that we do not need to invoke surface activity to account or the observed activation. Therefore, it is not really necessary here to introduce concentration and time dependent surface tension. For the HULIS samples, where surface tension does appear to play a role in activation, the extracted amounts were unfortunately too small for us to test the concentration dependence.

2) the application an “infinite” solubility to the different HULIS fractions in any concentration range (this is at least my understanding, since no specific solubility for the different fractions are indicated or discussed in the text).

Fulvic acid is highly water soluble. For example, aqueous solutions of SRFA obtained from the IHSS have been prepared at concentrations as high as 17.0 mg/mL (Diallo et al J Nanoparticle Research 2005) at several different pH values (5, 7 and 12). Hence, in the current experiment, we believe that the fulvic acid particles activate to droplets with no solid core. So far, probably due to the difficulty in sampling and extracting sufficient experimental material, water solubility of HULIS has not been tested (to our knowledge). In natural aerosol particles, the aqueous solubility of HULIS may be affected by high concentrations of salts. Testing activation and surface active behavior of HULIS-salt mixtures was beyond the scope of the current study.

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Diallo, M. S., Glinka, C. J., Goddard, W. A., Johnson, J. H. 2005. Characterization of nanoparticles and colloids in aquatic systems 1. Small angle neutron scattering investigations of Suwannee River fulvic acid aggregates in aqueous solutions. Journal of Nanoparticle Research 7 (4-5): 435-448.

3) I agree with the comments of the Anonymous Referee #2 expecting much higher concentration than 1 g/l in the growing droplets and underlying that this can strongly change surface tension effect on activation.

We agree that at the initial stage of activation the concentration may be high, thus resulting in lower equilibrium surface tensions. At higher concentrations, the rate of attainment of equilibrium surface tension is also faster than at lower concentrations. The dynamics of changes in surface tension and its concentration dependence are under investigation now and results will be shown in a forthcoming publication. However, please note that it is possible to account for the observed activation of SRFA using the surface tension value of water and the measured dissociation. For the HULIS we already deduced that surface tension effect may be important.

4) I would add, that this much higher concentration in growing droplets can also strongly limit solubility of HULIS.

We do not expect this to be the case, see previous comment (1 and 2).

5) So I think that the authors should discuss this limits and stress that this paper is a valuable tool for a relative comparison between SRFA and urban atmospheric HULIS

We added a sentence discussing these issues.

In addition some minor changes should be addressed

1) Please, state in the abstract that the investigated aerosol is of urban type (influenced by smoke conditions..) : it seems that different aerosol types, smoke and urban aerosol, were collected

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For the smoke particles, the samples were overwhelmingly dominated by smoke, as can be deduced from the atmospheric concentrations involved ($400 \mu\text{g}/\text{m}^3$ and $150 \mu\text{g}/\text{m}^3$) for the LBO-night and LBO-day samples, compared with less than $30 \mu\text{g}/\text{m}^3$ on regular days. For the pollution samples (3WKS) we have added a caveat.

2) It should be an error in the Abstract line 15-17, please rephrase it: activation diameters cannot be input parameter for accounting activation diameters! .

We thank the reviewer for this comment and changed the sentence in the abstract and it now reads: The Köhler model was found to account for activation diameters, provided that accurate physico-chemical parameters are known.

3) Introduction, pag 1075 line 14-16: please change “solubility” with “number of moles in solution” which depend on both solubility and molecular weight.

The reviewer is correct and this sentence has been changed.

4) Please change the title of section 2.2. in “Molecular weight fractionation of ”. Size fractionation is misleading.

We agree with the referee and changed the title of section 2.2.

5) Fig. 7: please add in the caption a short explanation of the legend.

This has been done, the revised version of the Figure 7 is now included.

6) Table 5: please add the units of activation diameters.

The units have been added to the table.

10) Figs. 5a, b and c can be replaced by one figure with symbols for measurements and different lines types for the different simulations . The same is valid for Figs. 6 and 7. This also makes possible the evaluation of the impact of different parameters directly on the graph.

We feel that the suggested figure will be too convoluted and decided to leave the figure

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as is.

11) I suggest a check the English by a mother language speaker, since the text, in some parts, is quite complicate to" follow"

Two of the authors are native English speakers. Also please note the comment of referee #2, praising the clarity of the manuscript.

Referee #2

The paper presents studies on the CCN activation of aerosols containing humic and fulvic acids. This is one of the first studies on the activation properties of these kind of compounds. Studied compounds were Suwannee River Fulvic Acid, used as a model compound for atmospheric humic-like substances, and three different types of aerosol samples from urban air. The paper is well written and presents results clearly. There are still some points that need clarifying and reconsideration.

Specific comments and questions: 1) In Abstract it is said that: 'The lower molecular weight fractions activated at lower critical diameters, which is explained by the greater number of solute species in the droplet with decreasing molecular weight.' This sentence is a bit confusing. By default, according to the Köhler-equation, the critical saturation of the aerosol particles decreases with decreasing molecular weight, which will lead to lower critical diameters (see e.g. Fig 6.), so why is this an important result?

This is a first study that shows that the molecular parameters of these species can be used in a Köhler equation to model the activation of these species. Molecular weight determination of these species is not trivial and our approach seems to be useful in extracting these parameters. We also show for the first time that the molecular weight is indeed the most important parameter for modeling the activation of these species. Therefore this is an important result and hence kept in the manuscript.

2) Surface tension measurements: The measurements were made for solutions of 1 g/L solutions. It seems that no dependence of surface tension on the organic concentration

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Discussion Paper

was determined, although the surface tension can be quite sensitive on the organic concentration. As it has been said in the manuscript (page 1093), the concentration of the organic is probably higher when the droplet is activated. I would expect the concentration to be 10 times (or more) higher than 1 g/L in some cases presented in the paper, maybe 10 times lower in some. Wouldn't it have been possible to make measurements on surface tension for other concentrations and get a rough estimate on the concentration dependence?

Please see reply to reviewer #1.

3) When calculated the dry activation diameter in Fig 6b, dissociation constant of 1.25 was used for all SRFA samples, where as in Table 4 the acidity of the different samples changes. Is it possible to do an estimate of the Van't Hoff factor for each sample? It seems that the acidity might explain the trend of measured dry activation diameters.

We explored the possibility that acidity may explain the activation trend, but did not observe any clear trend in acidity that could explain the activation trend better than by assuming a constant 1.25 van't Hoff factor. Therefore, for simplicity, we decided to retain the value of 1.25.

3) The studied compounds are assumed to be fully water soluble, with no solid phase in the droplets. Is there any information on the solubility of these compounds in water?

See reply to reviewer #1.

Technical corrections: 1) Page 1096, line 19. should be 'diafiltration'? The term has been changed.

In Table 5, the units are missing. This has been now corrected.

In Figure 6, the supersaturations are in wrong order. We thank the reviewer and the supersaturations are now in the correct order.

Reviewer #3

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This paper addresses the ability of model and atmospheric HULIS to act as cloud condensation nuclei. It is a timely and relevant scientific paper within the scope of ACP.CCN abilities of different molecular weight fractions of Suwannee River fulvic acid along with humic like substances extracted from atmospheric samples have been measured. The measured results are compared with predictions using classical Kohler theory and discussed in the context of atmospheric science. Efforts have been taken to address the effect of surface tension, molecular weight and dissociation factor. Some issues should however be addressed:

1) Solubility and particle phase. As also pointed out by referees 1 and 2 the number of moles of dissolved organic material in the droplet is determined by both molecular weight and water solubility. It seems an underlying assumption that activation is not limited by solubility. It should be possible to calculate the solubility limits for a solid phase to be important - based on back calculations using the parameters discussed in section 4.2 and the observed critical diameters. Could a solid core explain why the observed critical diameters are larger than the calculated values (using measured surface tension) in Figure 6c?

Sensitivity calculations proposed by the reviewer were performed. The results show that a solid core starts to increase the activation diameters (compared to the base case calculations) when the water-solubility of the organic matter is decreased below 1 mol/L. However, by postulating a solid core and varying the water-solubility to find an optimal fit to the measurements we could only improve the agreement with the measurements performed at a certain supersaturation while the discrepancies were inevitably increased in the case of the other supersaturations. Therefore postulating the presence of a solid core does not generally improve the agreement with the data. In particular, the presence of a solid core could not explain the partial overprediction of the measurements seen in Figure 6c.

See reply to reviewer #1. Also, since activation of SRFA can be accounted for by the estimated molecular weight, surface tension of water and a reasonable van't Hoff factor, it

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is suggestive that the SRFA fully dissolve. Also the activation curves at all supersaturations are well behaved for all size fractions, with no indications of dissolution problems, which would appear when comparing the different supersaturations. Finally, this study focused on water soluble material, at least at the solid:liquid ratios employed in the extraction procedure.

2) The dependence of surface tension on concentration has already been pointed out by referees 1 and 2 and should be addressed. Concentrations of organic material at activation could be estimated from Köhler theory using the parameters in tables 2 and 5.

The calculated concentration of organic material at activation varies between 20 and 170 g/L depending mainly on the water vapor supersaturation.

Minor comments/questions 3) Page 1080: What is the effect of the conditioning bulb? Are the results without the bulb different? The role of the conditioning bulb was to let the aerosols equilibrate with the environment (mostly by coagulation) and to allow the organics to diffuse to the surface and rearrange. The process is critical for these experiments as it leads to more homogenous particles and more reproducible results. This phenomena was also observed by us in hygroscopic growth experiments and recently during AMS experiments, where it was noticed that the size distribution narrows upon conditioning. The importance of aerosols generating procedure has recently been discussed by Zalanyuk et al.

Zelenyuk, A., et al. (2005), High precision density measurements of single particles: The density of metastable phases, *Aerosol Science And Technology*, 39, 972-986.

4) Page 1082 In lines 1-2 it says that the residence time of particles in the chamber were varied - what were the residence times in chamber?

The laminar flow in the chamber is dominated by the saturated sheath flow (800-970 cm³/min). We assume an average particle velocity which is constant and equal to ~0.65

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cm/sec (depended only on the chamber geometry and APS sample flow demand, 1 L/min), such that the particle residence time can vary between 15 to 43 sec depending on the injector position. In this work we have used residence times ranging from 15 sec for the highest supersaturation (1.03%) to 31 sec for lowest supersaturation (0.2%). This is now added to the text.

5) Please indicate which van't Hoff factor was used for ammonium sulfate

The calculations for ammonium sulfate are in Table 1. The Van't Hoff factor was calculated using a concentration-dependent parameterization presented by Young and Warren (Journal of the Atmospheric Sciences, 1138-1143, 49, 1992), which is now stated in the text.

6) Table 1: Are each of the points in figures 2 and 3 averages of 5-7 data points? This should be made clear

The error bars represent the standard deviation for each point of 6-14 experiments, on different days. This is now indicated in the text and in the figure captions.

7) Partitioning of surfactants is not taken into account in this work - this should be stated in the text.

A sentence is now added to the text and it now reads:

It should be noted that various individual compounds dissolved in the droplets are treated here as a single solute, and that partition of the compounds to the surface is not treated explicitly.

8) Page 1085 line 11: please define "apparent equilibrium".

We have changed the text, and it now states: We treat 90 minute values as equilibrium surface tension, although our time dependent measurements (not published) suggest that even at this long time, some solutions do not reach equilibrium with respect to surface tension .

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Minor technical comments 9) Page 1080, line 18 The sentence about the two DMAs should be rewritten - it says that the second DMA was used in scanning mode as an additional size selection step - it can not select size when used in scanning mode

The reviewer is correct and we changed it, and it is now: A second DMA (DMA-2, TSI-3080) was operated either as scanning mobility particle sizer (SMPS, coupled with a condensation particle counter (CPC, TSI-3022)) to verify the size distributions, or as an additional size selection step. . 10) The number of abbreviations used is quite large. To make the text easier to read I suggest that some of these words are written in full in the text (e.g. IOS, SubS, ST, HA)

We replaced the suggested abbreviations to the full words.

11) The use of MW and Mw (*W* as subscript in some cases) is a bit confusing, and it seems to me that it is not quite consistent; for example, Page 1086: MW is used in the sentence “is dominated by relatively small MW species” - I would assume that MW here would mean molecular weight? Page 1091: Mw is defined as the molar weight of the absorbing species, Page 1083 Mw is defined as the weight-averaged molecular weight, Page 1079 MW is introduced as the mean molecular weight, Page 1090 MW is used as integration parameter in an integration over the size distribution (the word size may be confusing)? Page 1085 it says that “there is no clear relationship between ST90 and MW” in Table 2 it says Mw?

We have now changed some of the abbreviations, and improved the consistency of the used terms.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 1073, 2006.

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