

Interactive comment on “Hygroscopic properties and cloud condensation nuclei activation of limonene-derived organosulfates and their mixtures with ammonium sulfate” by A. M. K. Hansen et al.

Anonymous Referee #1

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This contribution presents laboratory studies of particle hygroscopic growth and cloud drop formation of limonene generated organosulphates mixed with ammonium sulphate. Even though real atmospheric aerosols in general are composed of more complex mixtures, single compounds and simple mixtures of atmospherically relevant compounds still has to be studied in order to identify and test theoretical expressions and to evaluate relevant mechanisms. Hygroscopicity and cloud drop formation of many such simplified systems remain to be studied and organosulphates are key components in some of these.

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The experimental work is carefully done and in general well described (see minor comments below). The analysis is also scientifically sound and the conclusions are well supported in the work but I recommend the authors to carefully address the comments about particle composition below.

In many studies the theory used to account for surface tension is far too simplified and results in an overestimation of the role of surfactants in cloud drop formation. In this paper, several models are compared to illustrate this and it thus makes a significant contribution to the awareness of this effect.

I thus recommend publication after minor changes.

My main concern with the presentation relates to two effects that are discussed at several points in paper: 1) kappa values varying with particle size for subsaturation and 2) kappa values being higher than theoretically expected, especially for particles with 20-80% ammonium sulphate showing kappa values that are similar to those for pure ammonium sulphate. Both these effects depend on the assumption that the particle composition is as expected. This is mentioned in the text, but in the later discussion, the conclusion and the abstract, the possibility of deviations from the expected composition is not fully taken into account. A deviation could be due to several effects, for example surface to bulk or micelle partitioning in the atomizer or in the droplets formed or evaporation during drying (are vapour pressures for the organosulphates known?). I recommend that either the composition should be verified or the possibility of composition deviation should be accounted for in the conclusions and abstract.

As a possible reason for the size dependence of the hygroscopic growth, kinetic effects are discussed. I thus strongly recommend that details concerning the residence times in the DMAs and in the sampling lines before and after the humidifier are given.

Minor comments to the authors:

p. 17320 l. 17 the expression “activation diameter” can refer to either the droplet

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diameter corresponding to the maximum supersaturation in the Köhler curve, or to the minimum dry diameter for particles that can activate at a given supersaturation. Please clarify here and in the rest of the manuscript.

p. 17321 l. 14 The set-up used in this paper is referred to as "unique". In what way is it unique? Is it really the first time that hygroscopic growth and critical supersaturations are measured on the same aerosol?

p. 17323 l. 22 "unique", see above.

p. 17326 l. 2-5 From looking at the data, I guess that the procedure is to set one supersaturation and then scan over particle sizes to find the size for which 50% of the particles activate. This is not clearly described and I recommend changes to avoid miss-understandings and confusion.

p. 17326 l. 23-26 This could be explained in a more correct and pedagogical way. The kappa parameter is not primary size dependent, but composition dependent.

p. 17328 l. 23-25 Check the language.

p. 17330 l. 22-25 Check the language.

p. 17331 l. 13 "mixing ratios from 1-0" means 50-100% AS. Is this correct or do you mean 0-100% AS?

p. 17331 and figure 3. The deviation in the shape of the curve for surface tension as a function of concentration deviates from the theoretical expressions: according to experiments, most of the decrease takes place in the concentration interval 0.5 – 2,5 mmol/L. The deviation is discussed for the mixtures, but seems to be there also for the pure L-OS 250. Have you any idea why and if it has an effect on the surface to bulk partitioning?

p. 17332 l. 10 "There are no indications of deliquescence,..." Do you have the resolution in RH to observe a deliquescence? Also, for mixtures, no abrupt deliquescence

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step is expected, but rather a smooth increase in kappa values. Isn't this what is observed here?

p. 17332 l. 15-16 This could be interpreted as water solubility influencing the growth factors, while it only influences the deliquescence.

p. 17332 l. 27-28 "...any reduction of droplet surface tension from L-OS 250 should increase particle hygroscopicity." The effect of surface tension on particle hygroscopic growth is, however, very limited. Compare with p. 17341 l. 21-24 and figure 9, where there is almost no difference in the models with different surface tension expressions. Consider rephrasing these lines and the end of the paragraph.

Some of the discussion in sections 3.2, 3.3, and 3.4 would be stronger if the results of the modelling (Figure 9) were also taken into account.

p. 17336 l. 5-14 Was the bimodal size distribution observed in DMA 2b? If so, that would, as you mention, imply external mixture and deviations in composition. From my point it is difficult to see if the size dependence in kappa for pure AS is significant, but if so, it is surprising that it has not been observed before. Could there be measurement artefacts causing the size dependence: for example the parameterization of the dry particle correction between the DMAs or evaporation between DMA1 and DMA2a? In the end, I am not convinced about the conclusion that particle composition issues are not involved,

p. 17337 l. 19-20 The high molar weight and low dissociation (to a large extent independent of molecular structure) of L-OS 250 implies low kappa value. Solubility only influences kappa values in a small range of solubility; it is very much an on-off effect.

p. 17337 l. 20-22 What is the theoretical value of kappa for AS?

p. 17341 l. 15-18 This is an example of a conclusion that depends on the assumptions on particle composition.

p. 17342 l. 15-16 Check the language.

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p.17342 l. 27 Do you say that solubility influences kappa values for L-OS 250 at super-saturation? Is this consistent with -3/2 power dependence seen in figure 5.

p. 17343 l. 17-21 As the authors state, the additional hydroxyl groups may influence solubility, and may thus influence hygroscopicity at sub- or super-saturation. But an increased solubility, increasing the hygroscopic growth at subsaturation, may have no effect on the cloud droplet formation, since the concentration at activation is much lower than at subsaturation. Effects of solubility can thus not easily be extrapolated between sub- and super-saturation. It is therefore important to be specific when it comes to the humidity regime in which the changes are observed when it comes to solubility effects. Molar weight, in contrast, is expected to influence water up-take at sup- and super-saturations in similar ways. Please consider rephrasing.

p. 17345 l. 7-9 In my opinion, this conclusion depends on the composition assumption that has not been verified. Please consider rephrasing.

Thank you very much for interesting reading and an important contribution to science!

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