Overview:

The authors have provided a detailed and extensive account of laboratory measured hygroscopic properties and CCN activity of mixtures of ammonium sulphate and a limonene organosulphate they synthesised. Such aerosol models serve as suitable approximations for atmospherically relevant particulate matter. A single laboratory apparatus has been set up so that H-TDMA and CCNc measurements can be made in parallel the same aerosol source, thus minimising source dependent compositional discrepancies in the case of two separate units. The analysis was carried out using both H-TDMA and CCNc instruments so as to scrutinize the properties of interest in both sub- and super-saturated regimes.

In addition, they have provided modelled values of kappa for various formulations of bulk-surface partitioning and surface tension effects of the surface active organosulphate as well as kappa values derived from the ZSR mixing rule. It is clearly illustrated that the non-linear compositional dependency of kappa could not be described by the models indicating that while bulk-surface partitioning effects aerosol activation it is not driving the hygroscopicity. The validity of the ZSR additive mixing rule was scrutinized well and found to only be applicable for mixtures close to pure AS or LS-250.

The reviewer notes that there is a lack of motivation provided for the broader atmospheric scientific community, in particular why should global climate modellers take note, in the context of droplet activation and the indirect effect? The end of the introduction should clearly summarise the aims of the study, but it is also of great importance that the motivation for trying to achieve these goals is highlighted. κ is a particularly useful quantity for modellers, on all scales, as it facilitates a reduction in parameter complexity when describing aerosol chemistry. Placing a greater emphasis on the results obtained concerning κ in the context of climate modelling and implications for cloud-aerosol interactions will increase the impact of the paper.

The reviewer particularly notices, and commends, the attention given to errors and uncertainty throughout the paper.

The reviewer recommends the manuscript for publication subject to some minor revisions and consideration of some more general comments detailed below.

General comments:

1) The study employs various bulk-partitioning and surface tension considerations and the reviewer feels that this paper requires further referencing and attention to be given to the subject. While the a full account of the theoretical background is not necessary, the reviewer believes the paper will benefit an appendix or supplementary material section that outlines the assumptions, limitations, thermodynamic principles and corresponding key mathematical relationships (Gibbs adsorption isotherm) that underpin modelling such phenomena. In addition, there is extensive literature that has led to the development of such sophisticated bulk-surface partitioning models - see Sorjamaa et al. (2004)[1] and Topping et al. (2010, 2012)[2,3] – which remains uncited in the introduction, bulk text or conclusion here. In particular, Petters and Kreidenweis (2013)[4] carried out a surfactant study using a kappa parameterisation.

2) Some more discussion is required regarding the how reflective the composition of the aerosols in this study are of real atmospheric aerosols. In particular, can the author say that

the results found here, for laboratory-generated aerosols, are also true for much more complex aerosols mixtures that are present in the atmosphere?

3) While the paper is indeed readable, the English could be better. Please read through the manuscript again with this in mind and adjust the grammar accordingly so as to improve the readability of the paper.

4) A more detailed explanation of exactly how the κ values are derived from the H-TDMA and CCNc measurements is required.

5) In figure 5 there are two fewer data points for the pure L-OS 250 curve when compared with mixtures and pure AS. This is again evident in figures 7 and 9. Please add to the main text why this is the case.

6) It is not transparent how κ values are modelled in 3.4.4, please detail further in the text how this is done. Adding additional equations if necessary. In particular, it is not immediately clear to me how one models the κ from modelled HGF/SSc. As I understand it, one must know HGF/SSc to back out κ (from equations 5/6) or vice versa. In the case of the supersaturated regime, please add equation for SSc (i.e. Köhler curve maximum) in terms of κ. Perhaps you mean to say experimentally derived HGF/SSc values are used to model κ? This is unclear to me, please clarify and add to text.

7) In section 4 it should be highlighted that the CCNc measurements are of greater importance for cloud formation owing to supersaturation in clouds. In addition, some discussion is required here for the implications of your results for global climate models. Specifically, please add Prisle et al. 2012[5] reference to this section whilst noting that σ_b is a particularly erroneous representation for global simulations of droplet activation and link to your results presented in figure 9. Please also comment explicitly on the whether you expect there to be significant sensitivity of droplet concentrations if organosulfates are included as a separate compound in global climate models or can they be aggregated with general organics? Relate also to organic and organosulfate κ values.

<u>Minor revisions:</u>

Section 2.2: Are surface tensions taken after reaching steady state, equilibrium values? See and reference Nozière et al. (2014)[6].

Section 2.2: Equation 1 is missing $d\sigma/dm_{inorganic}$ term from cited paper. Please find alternative reference for equation or explain why this term vanishes here. Also, it's not necessary to explain 'ln' to the reader, "Ln is the natural logarithm (to the base of e)", and state that molar concentration is the bulk quantity.

Page 17320 line 17: Please define activation diameter. In different literature this can refer to the wet diameter that corresponds to the maximum of a given Köhler curve or to the dry diameter of the smallest aerosol size that can be classified as a CCN for a given supersaturation. It should be the latter.

Page 17324 line 15: “Dry gas (N_2) was applied after atomization to dilute the particle concentration.” – The casual reader, not familiar with this kind of experiment, may not know why this is required, please explain.

Page 17324 line 28: “Number size distribution” should be “Number concentration size distribution”.

Page 17325 line 16: “Error bars presented in the following sections on reflect the variations between these measurements according to the observed relative standard deviations (±2 standard deviation).” Poor English – “Error bars presented in the following sections reflect the variation in measurements according to observed relative standard deviations (±2 standard deviation).”

Page 17325 line 24: Incorrect figure reference – please change to Fig. 2.

Page 17325 line 25: “Monodisperse”, are these the same four sizes as used in H-TDMA? Unclear.

Page 17326 line 1: 1 micrometre is not the only definition for cloud droplet classification. This can also be defined in terms of the dry activation diameter or the critical supersaturation; this is worth mentioning for the droplet activation community.

Page 17326 line 3: There has been no mention of the supersaturation band calibration yet, that should come prior to this for clarity – it’s not clear at this stage that these are the calibrated values.

Page 17326 line 18: Please define critical particle diameter.

Page 17327 line 23: While I follow the logic of capturing surface tension effects in kappa, I’m not familiar with this method, nor will the average reader be, I feel this requires some elaboration, validation or a word of caution (if it can’t be referenced from another study).

Page 17328 line 6: Please state that pure component kappa values will be taken to be mean measured values.

Page 17328 line 23: “Equilibrium growth by water uptake and cloud droplet activation of the studied particles from Köhler theory as described in Prisle et al. (2010b). “ change to “Equilibrium growth by water uptake and cloud droplet activation of the studied particles is calculated from Köhler theory as described in Prisle et al. (2010b).”

Page 17328 line 24: Remove “*following*”.

Page 17328 line 25: First instance of SSc abbreviation, please write in full. Abbreviation introduced on page 17334 line 1, only use abbreviation there.

Page 17329 line 7: It is not clear what the ‘b’ refers to in ‘σ_b’ making it easy for the reader to forget which partitioning scheme this is referring to. Please change or state what the ‘b’ stands for.

Page 17329 line 10: remove parentheses and replace with “and thus kappa and droplet surface tension”.

Page 17329 line 15: Please add reference or justification for no dissociation of L-OS250 (or similar organic compound).

Page 17331 line 13: “*mixing ratios from 1-0”* suggests half AS and half LS-250 to pure AS. Please change.

Page 17331 line 19: It seems these fitting parameters are used for all compositions, is that correct? This is doesn't seem logical, can't these be revaluated for each w/w% composition? Please also add R^2 values for quantitative illustration of the ability (or inability) of equation 1 to capture the surface tension depression effect. Different fitting parameters and corresponding R^2 values should be collected in a table.

Page 17332 line 16: As the lowest subsaturated RH value explored is approximately equal to the DRH we don't see the deliquescence action in the results here. If additional measurements were taken at 75% RH, for example, we would hope to see the deliquescence manifest itself in the HGF between that data point and one at 80% RH.

Page 17334 line 9: "The curves for all six compositions follow the Köhler slope of approximately −3/2 in log-log space" contradicts sentence starting line 12 "Pure AS and L-OS 250 with 80, 50 and 20 % w/w AS had a slope of −3/2, whereas the slope for pure L-OS 250 and L-OS 250 with 10 % w/w AS were slightly smaller (approximately −1.4)".

Page 17336 line 20: Define $\Delta\kappa = \kappa 93 - \kappa 80$.

Page 17337 line 28: I don't see this trend. One *might* argue that a minimal trend *might* be present for pure L-OS 250; however, in the case of the 10% w/w AS mixture, the variability in κ_{CCN} between the first and last data points is too large to conclude that there is a trend. Please revise.

Page 17339 line 13: *"An exception is found for pure AS at 90 % RH, and L-OS 250 with 20 to 80 % w/w AS at 93 % RH, where* $\kappa_{H\text{-}TDMA}$ *were below* κ_{CCN} *for the three larger 15 particle sizes."* If possible, please add a hypothesis as to why this might be the case.

Page 17339 line 24: It would be instructive to specify the residence time of the instrumentation to provide transparency regarding any kinetic effects that may be present.

Page 17340 line 6: "extend" should be "extent".

Page 17341 line 8: should read "upper left"

Page 17341 line 27: "non-ideal droplet interaction effects", are these internal droplet mixture effects? This terminology is not familiar to the reviewer and is therefore most likely not familiar to the average reader, please revise or explain.

<u>Minor comments regarding figures:</u>

Figure 1: Please add stoichiometric coefficients if possible.

Figure 8: Please change x-axis tick resolution to match y-axis. Rephrase "as a function" neither derived value of kappa is a function of the other.

Figure 9: Add modelled values to legend. Add space between "modelled" and "κ".

<u>References</u>:

[1]:Sorjamaa, R., Svenningsson, B., Raatikainen, T., Henning, S., Bilde, M., and Laaksonen, A.: The role of surfactants in Kohler theory reconsidered, Atmos. Chem. Phys., 4, 2107–2117, 2004.

[2] :Topping, D.: An analytical solution to calculate bulk mole fractions for any number of components in aerosol droplets after considering partitioning to a surface layer, Geosci. Model Dev., 3, 635– 642, doi:10.5194/gmd-3-635-2010, 2010.

[3] :Topping, D. O. and McFiggans, G.: Tight coupling of particle size, number and composition in atmospheric cloud droplet activation, Atmos. Chem. Phys., 12, 3253–3260, doi:10.5194/acp-12-3253- 2012, 2012.

[4] : Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity – Part 3: Including surfactant partitioning, Atmos. Chem. Phys., 13, 1081–1091, doi:10.5194/acp-13-1081-2013, 2013.

[5] :Prisle, N. L., Asmi, A., Topping, D., Partanen, A.-I., Romakkaniemi, S., Dal Maso, M., Kulmala, M., Laaksonen, A. , Lehtinen, K. E. J., McFiggans, G., and Kokkola, H.: Surfactant effects in global simulations of cloud droplet activation, Geophys. Res. Lett., 39, L05802, doi:10.1029/2011GL050467, 2012.

[6] : Noziere, B., Baduel, C., and Jaffrezo, J. L.: The dynamic surface tension of atmospheric aerosol surfactants reveals new aspects of cloud activation, Nature Communications, 5, 3335– 3342, doi:10.1038/ncomms4335, 2014.