

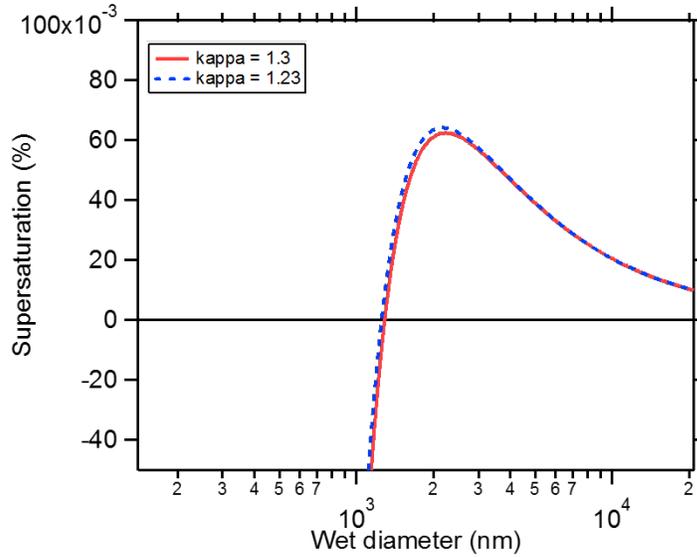
Response to Reviewer #1

We thank the reviewer for the thoughtful comments. We address each comment individually below, with the reviewers initial comment in **black** and our responses in **blue**.

The authors present a comprehensive study on the potential role of a subset of surfactant molecules in dictating aerosol activation behavior. This is an issue that waxes and wanes in the literature, with no consistent theoretical framework or set of standards for comparisons. I appreciate the brief summary of studies presented and I enjoyed digesting the results. In many occasions I found myself deleting a specific point to raise that was answered further in the document. Indeed, the small number of questions raised below reflects this. The authors have considered multiple angles and it is certainly worthy of publication in ACP. I would appreciate that, prior to publication, a number of general issues are clarified. For studies with relatively low number of compounds, theoretical results are more sensitive to variations in pure component and mixture properties. These issues might have arisen from a confused interpretation on my part, but are important to consider given the varying prescribed importance of this area of study.

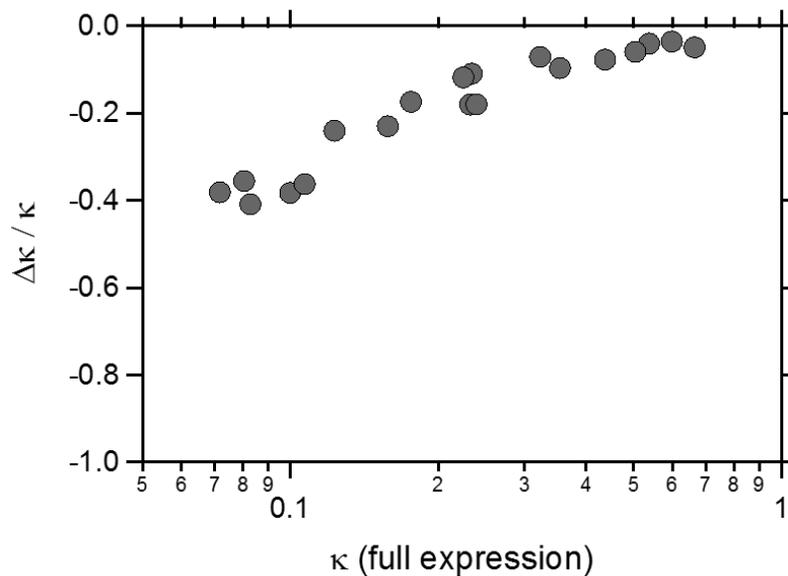
Section 2.2 Kappa values are not constant with changing water content due to nonideal mixing. A value of 1.33 assumes ideality, presumably, whilst Kappa values for Sodium Chloride, theoretically, stride from ~1.5 to 1.23 as RH increases from 90 to 99%RH. Does this affect the methodology for RH calibration? Would this change figure 5B.

The reviewer raises an important question about the value of kappa that is used here. Indeed, kappa is not fundamentally a constant but varies with RH due to changes in activity. The numbers given by the reviewer are consistent with those calculated from the UManSysProp (<http://umansysprop.seaes.manchester.ac.uk/>) online tool, using the “Hygroscopic Growth Factors” (HGF) tool. When the “CCN Activation Potential” tool is used the kappa values at the point of activation can be calculated. These calculations indicate that above 99% RH (the upper limit in the “HGF” tool) the kappa values for NaCl again increase and depend on the size of the dry particle, increasing with particle size. For the vast majority of experiments in our study, including calibration experiments, the dry particle size was 180 nm. The UManSysProp calculations indicate that kappa = 1.295 for 150 nm and 1.30 for 180 nm dry particles at the point of activation, RH = 100.04%. This is identical to the value of 1.30 assumed by us. The calibrations occur at > 99% RH for the CFSTGC, typically 99.9% or so (see Figure S1). And the calibrations for the CCN instrument are at >100% RH. Thus, the value of 1.3 is generally reasonable for the conditions here. Further, we can assess the impact of kappa being somewhat smaller, specifically equal to the value at 99% RH (= 1.23). The critical supersaturation would change from 0.0624% (using kappa = 1.3) to 0.0642% (using kappa = 1.23). This is illustrated in the figure below. The difference is exceptionally small, and would not impact our general or specific conclusions. In our revised manuscript, we intend to make note of this issue.



Equation 2, as used from the Petters and Kreidenweis 2007 paper, is referenced as being valid in that original source when Kappa > 0.2. However, in this study you presented derived Kappa values < 0.02 even for the oxidised test case. I would like to see presentation of why this assumption is not important.

To test this assumption we have recalculated the kappa values using the full expression, where the kappa is derived from the critical supersaturation using Eqn. 6 in Petters and Kreidenweis (2007), i.e. from the full Kohler curve. We find that the difference between the kappa from the full expression differs negligibly from that using the approximation (Eqn. 2), with a maximum difference of <0.5% (corresponding to $\Delta\kappa \sim 0.0004$) of the actual kappa (see figure below). Thus, we see that this assumption is not important, at least for the experiments here. In our revised manuscript we intend to make note of this issue.



More generally, I'm unsure if the role of activity coefficients in dilute solutions might somehow affect any re-partitioning, assumptions of ideal mixing in equation 4, or raise the potential for LLE in the systems studied here. Could the authors comment?

And

Section 3.4 Following the previous comments, for the oxidation experiments the authors note that all of the organic mass could be accounted for by three compounds [86+7+7]. All of these compounds still have low κ values, the highest < 0.02 . Multiple studies rely on the potential for LLE to explain any variation in observed hygroscopicity. Given the often high mass fractions of total organic in these studies, I re-iterate if the authors have considered any contribution from a possible LLE, with unknown morphology, that might introduce errors associated with the approach presented here.

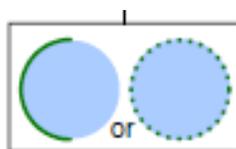
LLE (liquid-liquid equilibrium) or equivalently liquid-liquid phase separation (LLPS). Quoting Ovadnevaite *et al.* (2017), "Liquid-liquid phase separation emerges as a consequence of a substantial degree of non-ideal mixing to the point where the formation of an additional phase becomes thermodynamically favourable (stable liquid-liquid equilibrium state) in comparison to a single, homogenous liquid phase." Very likely LLPS is playing a role for the systems investigated here, with an aqueous-rich phase and an organic-rich phase occurring. Various studies have established that LLPS readily occurs for organic-salt systems when the O:C of the organic compound or mixture is less than ~ 0.6 (e.g. Bertram *et al.*, 2011; Song *et al.*, 2012). The O:C of the fatty acids (prior to oxidation) used in our study are < 0.15 . Thus, we fully expect LLPS to occur.

To a reasonable extent, our assumption in the "upper limit" surface tension case is effectively a statement of there being two phases, i.e. of LLPS: an inorganic-aqueous core and an organic shell, the thickness of which depends on the amount of organic and the size of the droplet. This is, in essence, equal to the "model III" in Ovadnevaite *et al.* (2017). As they describe it, in their simplified organic film model "all organic material resides in a water-free insoluble organic film adsorbed to an aqueous, salt-rich core phase, coating the core phase completely up to the point where a minimum thickness δ_{org} ($\delta\beta$, min in our model) is reached. Hence, this simplified model resembles our more complex thermodynamic equilibrium model with LLPS, but with two major differences: (1) no organic material dissolves into the growing aqueous phase and (2) no water partitions to the organic film 'phase', that is, a permanent and complete organic-inorganic LLPS at all relative humidity levels." The compressed film model is ultimately just a variation on this same idea, but that allows for some dissolution of the organic in the aqueous, salt-rich core phase at high coverage and that specifies a relationship between the achievable surface tension and bulk concentration (Eqn's 7 & 8 in our paper).

So, in essence, we have considered LLPS. We have not explicitly considered the issue of "unknown morphology," but to the extent that morphology is even really reflected in our model it is in the parameters that are derived. We calculate, for example, molecular area assuming that the organic phase is equally present across the entire droplet surface. We could have alternatively assumed that the organic phase covered e.g. only half of the droplet, making a hemisphere (illustrated in the cartoon below, taken from Ovadnevaite *et al.* (2017)). Or "molecular islands" could form as the droplet grows and the surface coverage decreases, leaving organic-rich patches where the surface tension remains reduced even if the overall coverage, calculated based on the total surface area of the droplet, is low. Had we done this the molecular area values would change and we would have to calculate the effective surface tension of the droplet as some weighted average of the surfaces exposed to air (i.e. the organic-

air interface and the water-air interface). This would result in shifts in the molecular area term, and in particular the critical molecular area. And if we calculated the surface tension of just the organic-air interface we would obtain values that would deviate from that obtained assuming full surface coverage, with the “hemisphere” values being smaller for a given total coverage (to maintain the overall average surface tension). Put another way, we fully expect that a more thorough consideration of impacts of morphology (e.g. “islands”) would lead us to the same general conclusions, but the derived molecular parameters might change. That said, given that for the oleic acid + salt system we find that the derived surface pressure isotherms are quite similar to bulk experiments, there is no strong reason to think that, at least for the single organic component systems considered here, that the introduction of a more complex morphology model, with unknown parameters, would be beneficial.

In our revised manuscript, we will briefly discuss the relationship between the models that we have used here and the concept of liquid-liquid phase separation.



Section 2.5. Perhaps I’ve interpreted this section incorrectly, but how are variables used in the fitting process constrained?

Only the variables A_0 , m_σ , and C_0 are allowed to vary during the fitting process. (Other variables are inputs from the observations). The individual parameters are not explicitly constrained beyond reasonable physical constraints. In particular, all three parameters are constrained to be > 0 . However, in a practical sense we have not found it necessary to actually impose these constraints during the data fitting since the natural solution has these parameters in their physically realistic ranges. We do, however, constrain the surface tension to be > 0 mN/m. We will make note in the revised manuscript that the parameters are constrained to be within physically reasonable ranges.

Section 3.3 For such high mass fractions, how would any solubility limitations affect results from assuming an ideal kappa-mixing rule?

We may be misinterpreting this question, but we explicitly assume that the organic material is effectively insoluble in water ($\kappa = 0.001$) and thus there are not really “solubility limitations.” In the ideal mixing case, the difference between $\kappa = 0$ and $\kappa = 0.001$ is negligible and unnoticeable on a figure such as Fig. 5a. However, to the extent that the organic material is actually somewhat more soluble than we assumed at the high mass fractions, we would expect the calculated κ from ideal mixing to be too low. In other words, the line shown in figure 5a can be taken as a lower limit.

Minor comments: Page 11, line 7: Please correct ‘The surface tension is constrained by always be larger than some minimum value...’

Done.

References:

- Bertram, A. K., Martin, S. T., Hanna, S. J., Smith, M. L., Bodsworth, A., Chen, Q., et al. (2011), Predicting the relative humidities of liquid-liquid phase separation, efflorescence, and deliquescence of mixed particles of ammonium sulfate, organic material, and water using the organic-to-sulfate mass ratio of the particle and the oxygen-to-carbon elemental ratio of the organic component, *Atmos. Chem. Phys.*, *11*(21), 10995-11006. <https://doi.org/10.5194/acp-11-10995-2011>
- Ovadnevaite, J., Zuend, A., Laaksonen, A., Sanchez, K. J., Roberts, G., Ceburnis, D., et al. (2017), Surface tension prevails over solute effect in organic-influenced cloud droplet activation, *Nature*, *546*(7660), 637-641. <https://doi.org/10.1038/nature22806>
- Song, M., Marcolli, C., Krieger, U. K., Zuend, A., & Peter, T. (2012), Liquid-liquid phase separation in aerosol particles: Dependence on O:C, organic functionalities, and compositional complexity, *Geophysical Research Letters*, *39*(19). <https://doi.org/10.1029/2012GL052807>