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Interactive comment on "Technical Note: The Role of Evolving Surface Tension in the Formation of Cloud Droplets" *by* J. F. Davies et al.

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The technical note summarizes a set of interesting points to be clarified regarding the role of surface active organic aerosol in cloud activation. In light of several recent works, including those of the authors, this topic is very timely and their call for a discussion on the topic is commendable. While it is useful on occasion to summarize the knowledge and open questions in the field, my main concern is that the note brings very little new to the table. Most or all of the points have been made previously, but little references or perspective is given to the substantial body of work already existing on the subject. Some examples are:

p.2 l. 36-38: "In this note, we focus on the role of surface tension, and discuss the limitations of current approximations in light of recently published works that reveal how it is primarily the evolution of surface tension that impacts the activation process." Only

two papers are discussed in detail, the works of Ruehl et al. (2016) and Ovadnevaite et al. (2017). The discussion is not sufficiently substantiated independently of these works.

p.3 l.72-75: Effects of inorganic co-solutes is discussed by e.g. Svenningsson et al. (2006), Prisle et al. (2010,2011), Frosch et al. (2011), Kristensen et al. (2014), and Hansen et al. (2015). Effects of dissolution is discussed by e.g. Shulman et al. (1996) and Bilde and Svenningsson (2004).

p.4. l.81: "…there are many observations that cannot be explained in such simple terms". Please be specific, which observations cannot be explained and what is the argument that they are unexplained.

p. 5-6 and Fig. 1(A): A substantial part of the manuscript is devoted to explaining basic Köhler theory, as done by many authors previously, including basic textbook material. The presentation could benefit from a similarly detailed presentation of the surface tension and partitioning models used.

p.7 l. 171-72: "This also seemingly supports previous assertions that surface tension does not impact activation, since it is generally argued that at the point of activation the droplet is sufficiently dilute and essentially exhibits a surface tension like pure water." Please reference a sufficient amount of such previous assertions to support the claim of a general argument.

p.8 l.180: "… knowing the surface tension only at the point of activation is in sufficient to determine the critical properties at activation…" Please provide references.

p.11 l.258-64: "This predicted size effect indicates that it is not generally valid to assume that all activating CCN will have a surface tension equivalent to or close to that of pure water –nor is it appropriate to use a single measurement of the surface tension of a multicomponent CCN of known dry composition at its activation size (only) to determine its Köhler curve. Furthermore, these model predictions also suggest that measurements of the surface tension of larger CCN particles (e.g. > 150 nm dry diameter) may not allow for conclusions about the surface tension of much smaller CCN, e.g. of 50 nm dry diameter." These points have certainly been made by other studies than the one specifically described, including those mentioned above, and Wittbom et al. (2018). A broader perspective should be provided.

p.12 l. 292-92: "…in contrast to other studies that allow both coated particle size and organic volume fraction to vary simultaneously." Although in many studies particles are produced by other methods than coating (e.g. nebulization), again many other works have indeed recognized the importance of independently varying the particle size and organic fraction, for studying the effects of organic surface activity and mixing effects, including those listed above.

p.13 l.310-12: "One could ignore the physical meaning of K and simply use it as an all-encompassing parameter to describe activation efficiency." This was already done by several previous studies, e.g. Kristensen et al. (2014) and Hansen et al. (2015). I do understand that the authors caution against it, but see also my points below.

p.13 l.312-13: "In this case, the generality of the parameter to interpret observations in different conditions is lost." Please explain what is meant by this statement, and how that would not be the case by separating out surface tension from the K parameter. Please give references to previous work debating this, as well as to the original work of Petters and Kreidenweis (2007) and following articles to support why this is not the proper way to interpret their presented framework.

p.13 l.318-19: "… a specific suberic acid hygroscopicity alone cannot explain the observations across a range of particle sizes and compositions" That was also found for other well-defined organic aerosol by e.g. Kristensen et al. (2014), Hansen et al. (2015), and Wittbom et al. (2018). Indications of similar relations have been seen for ambient aerosol by e.g. Hong et al. (2014,2015).

p.15 l.349-50: "…all organic material is assumed to reside in a water-free organic

shell-phase (an organic film) at the surface of the aqueous droplet." This assumption was also used by e.g. Prisle et al. (2011).

p.15 l.349-50: "…neither of the models fully captures the observed behavior at all forg and size regimes." Previous studies have made similar conclusions for other aerosol and other models, please bring these into perspective to present a broader perspective of the issue.

p.17 l.399-400: "Surface tension effects can lead to significant differences from classic, hygroscopicity mixing rule mechanisms for CCN activation." This was also seen by Kristensen et al. (2014) and Hansen et al. (2015), among others.

p.30: For example Shulman et al. (1996), Sorjamaa et al. (2004), and Prisle et al. (2008) present similar Köhler curves. Please discuss Fig. A2 in context of previous results.

The most significant novelty of this work lies in the measurements presented in Fig. 3, but these results lack a comprehensive discussion. Significantly more novel content should be added to the work before publication. For example, no explanation is given for the variation between the salt seeds and no modeling is done to provide interpretation beyond general speculation. Would it not be possible and facilitating to the discussion to make model predictions using exactly the outlined framework, for these aerosol? CCN activation experiments could be made with the systematic variation in particle size and organic fraction which this technical note specifically calls for. How are the impacts on water activity from the different salts treated in the model? Could intrinsic salt hygroscopicity/solubility explain the variation with mass fraction, and if not, why? More generally, a discussion could be added on the atmospheric/organic aerosol process relevance of suberic acid and mixtures with each of the salts.

For the model part, I commend the effort to use a more general activity model for calculating the Köhler curves. This is indeed one of the major sources of discussion related to identifying surface tension effects in Köhler theory. However, the use data presented in Table 1 is not sufficiently justified. For example, why was the 20 C values used? What is the basis for assuming similar surface tension based on structural similarity? For other compounds, small changes in molecular length can lead to greatly enhanced surface activity. How did Riipinen et al. make the determination of the pure compound value? How is pure ammonium sulfate (a solid at 20 C) surface tension justified? How is the minimum shell thickness estimated?

What would be the impact on Köhler curves using more mixture specific input data? Can the authors rule out that any of the effects described are not caused by solution non-ideality and misrepresentation of the experimental system by use of incompatible thermodynamic data? It would strengthen the arguments significantly to use accurate reference input data if such may be obtained from a thorough literature search, or from performing new measurements for the specific systems in question. The lack of proper input data for different Köhler models is a major limitation of obtaining a comprehensive molecular framework, as called for in this technical note – this would be one of my first additions to the discussion.

The discussion about discontinuities in the activation curves is very interesting. It would be useful to see Fig. 1(B) developed for somewhat more realistic conditions. Specifically, do similar discontinuities persist in Köhler curves when concentration dependent partitioning is taken into account? What are the relation between the curves in Fig. 1(B) and A2? Why do they look different?

The present technical note draws primarily on the previous work of Ruehl et al. (2014,2016). It should be made clearer which results are summarized from there, and which are new for this work.

The presentation and arguments would benefit greatly from an independent presentation of the model framework and main assumptions used. In particular, it is not entirely clear what partitioning framework is used and how the surface composition is actually evaluated. It is not clear how mutually different the employed frameworks are, that is,

how wide a range of possible representations of the aerosol are mapped with the three different models used. As the majority of previous work uses a Gibbs-based partitioning model, would it not make sense to include such calculations in the comparison? The results in Fig. A2 could be discussed in greater depth, as could the statement "... the simplified organic film model provides the best description of these experimental data" p. 16 l.374. Why was the "best framework" not verified by e.g. measuring the droplets size at various equilibrated RH?

Specific comments.

p.3. l.66: What is meant by "vastly different"?

Fig. 2: Why are results shown for different values of Korg (dashed line) in panels A, B, and C?

Fig. 3: How are experimental error bars estimated?

Fig A2: What causes the kink in (presumably) the pure water surface tension curve in (e)?

References:

Michelle L. Shulman, Michael C. Jacobson, Robert J. Carlson, Robert E. Synovec, and Toby E. Young: Dissolution behavior and surface tension effects of organic compounds in nucleating cloud droplets, Geophys Res Lett 23, 277-280, 1996.

Sorjamaa, R., Svenningsson, B., Raatikainen, T., Henning, S., Bilde, M., and Laaksonen, A.: The role of surfactants in Köhler theory reconsidered, Atmos. Chem. Phys., 4, 2107-2117, https://doi.org/10.5194/acp-4-2107-2004, 2004.

Svenningsson, B., Rissler, J., Swietlicki, E., Mircea, M., Bilde, M., Facchini, M. C., Decesari, S., Fuzzi, S., Zhou, J., Mønster, J., and Rosenørn, T.: Hygroscopic growth and critical supersaturations for mixed aerosol particles of inorganic and organic compounds of atmospheric relevance, Atmos. Chem. Phys., 6, 1937-1952, https://doi.org/10.5194/acp-6-1937-2006, 2006.

Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, Atmos. Chem. Phys., 7, 1961-1971, https://doi.org/10.5194/acp-7-1961-2007, 2007.

N. L. Prisle, T. Raatikainen, R. Sorjamaa, B. Svenningsson, A. Laaksonen and M. Bilde (2008): Surfactant partitioning in cloud droplet activation: a study of C8, C10, C12 and C14 normal fatty acid sodium salts, Tellus, 60B, 416-431, DOI: 10.1111/j.1600-0889.2008.00352.x.

Prisle, N. L., Raatikainen, T., Laaksonen, A., and Bilde, M.: Surfactants in cloud droplet activation: mixed organic-inorganic particles, Atmos. Chem. Phys., 10, 5663-5683, https://doi.org/10.5194/acp-10-5663-2010, 2010.

M. Frosch, N. L. Prisle, M. Bilde, Z. Varga and G. Kiss (2011): Joint effect of organic acids and inorganic salts on cloud droplet activation, Atmospheric Chemistry and Physics, 11, 3895-3911, doi: 10.5194/acp-11-3895-2011.

T. B. Kristensen, N. L. Prisle, and M. Bilde: Cloud droplet activation of mixed model HULIS and NaCl particles: Experimental results and κ-Köhler theory, Atmospheric Research, 137, 167–175, 2014, DOI: 10.1016/j.atmosres.2013.09.017.

Hong, J., Häkkinen, S. A. K., Paramonov, M., Äijälä, M., Hakala, J., Nieminen, T., Mikkilä, J., Prisle, N. L., Kulmala, M., Riipinen, I., Bilde, M., Kerminen, V.-M., and Petäjä, T.: Hygroscopicity, CCN and volatility properties of submicron atmospheric aerosol in a boreal forest environment during the summer of 2010, Atmos. Chem. Phys., 14, 4733-4748, https://doi.org/10.5194/acp-14-4733-2014, 2014.

Hansen, A. M. K., Hong, J., Raatikainen, T., Kristensen, K., Ylisirniö, A., Virtanen, A., Petäjä, T., Glasius, M., and Prisle, N. L.: Hygroscopic properties and cloud condensation nuclei activation of limonene-derived organosulfates and their mixtures with ammonium sulfate, Atmos. Chem. Phys., 15, 14071-14089, https://doi.org/10.5194/acp-

15-14071-2015, 2015.

Hong, J., Kim, J., Nieminen, T., Duplissy, J., Ehn, M., Äijälä, M., Hao, L. Q., Nie, W., Sarnela, N., Prisle, N. L., Kulmala, M., Virtanen, A., Petäjä, T., and Kerminen, V.-M.: Relating the hygroscopic properties of submicron aerosol to both gas- and particle-phase chemical composition in a boreal forest environment, Atmos. Chem. Phys., 15, 11999-12009, https://doi.org/10.5194/acp-15-11999-2015, 2015.

Wittbom, C., Eriksson, A.C., Rissler, J. et al. J Atmos Chem (2018). https://doi.org/10.1007/s10874-018-9380-5

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