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Dear Jingkun:

Thank you for your effort in guiding the initial review for our paper “Interaction between Dicarboxylic Acid and Sulfuric Acid-Base Clusters Enhances New Particle Formation” (acp-2018-975) by Lin et al. We also appreciated the additional comments from both reviewers. Most of the comments by the reviewers were helpful, and we have revised the paper accordingly. Our point-by-point responses to the reviewer’s comments are included below.

Thank you again for your assistance.

Sincerely, Renyi Zhang

Reviewer #1

This is a revised manuscript regarding the interaction between succinic acid and clusters consisting of sulfuric acid-ammonia/dimethylamine in the presence of water molecules using quantum chemical calculation methods under the umbrella of atmospheric new particle formation. Although the quality of this manuscript has significantly improved after the revision, a few concerns remain to be addressed.

1. The author lists in the main manuscript and the supplement should match.

Modified as suggested.

2. Since succinic acid is the only dicarboxylic acid that has been studied, the authors are advised to use "succinic acid" instead of "dicarboxylic acid" in the title.

The title has been changed into "Interaction between Succinic Acid and Sulfuric Acid-Base Clusters".

3. Double check the numbers in Table 6, a number of clusters come with concentrations less than 1 cm-3. Although the authors stated that steady-state equilibrium for clusters is rarely established, these numbers are way too low. Extending to the ratios in Table 7, the current number, if true, really suggests that succinic acid pathway is unimportant either.

The calculations have been double-checked as suggested. We have added the following on p. 17, "The estimated cluster concentrations using eq. 9 and the atmospherically relevant concentrations of the precursor species are 10^{-3} ~10^{2} cm^{-3} for SA•DMA •SUA and 10^{0} ~10^{3} cm^{-3} for SA•SUA (Table 6), suggesting that SUA likely contributes to the further growth of the SA and SA•base clusters.". In addition, we have provided more description on the cluster formation and evaporation on p.17 "Under atmospheric conditions, the cluster growth can be represented by a reversible, stepwise kinetic process in a single or multi-component system,

$$\ldots C_{i-1} \underset{k_i^-}{\overset{+A_{i-1},k_{i-1}^+}{\rightleftarrows}} C_i \underset{k_{i+1}^-}{\overset{+A_i,k_i^+}{\rightleftarrows}} C_{i+1} \ldots \tag{10}$$

where A_{i-1} denotes a monomer species to be added to the cluster C_{i-1} at the $(i-1)^{th}$ step and k_i^- and k_i^+ represent the association and decomposition rate constants of the cluster, respectively. Hence, whether cluster C_i grows or decomposes is dependent on the competition between the forward and backward reactions for C_i, which are dependent on the rate constant k_i^+ and monomer concentration $[A_i]$ and k_i^- (i.e., the thermal stability of C_i, respectively (Zhang et al., 2012). The time-dependent concentration of cluster C_i is derived from the equation,

$$\frac{d[C_i]}{dt} = k_{i-1}^+[C_{i-1}][A_{i-1}] - k_i^-[C_i] - k_i^+[C_i][A_i] + k_{i+1}^-[C_{i+1}] \tag{11}$$

Note that the eq. 9 is the sum of the steady-state expression of eq.11 over all reaction steps". And on p. 18-19 "It should be pointed out that steady-state equilibrium for pre-nucleation clusters is rarely established under atmospheric conditions for each intermediate step (i.e., eq. 11) and the overall reaction (i.e., eq. 9) of the cluster formation, … Hence, the clusters grow (or evaporate) when $k_i^+[A_i]$ is larger (smaller) than k_i^- (eq. 11) … Furthermore, in addition to SUA, there are many other organic acids particularly those with more functionality, i.e., more carboxylic acid groups and the presence of hydroxyl groups, that also likely contribute to aerosol nucleation".

Reviewer #2

The authors have made substantial changes to the manuscript in response to comments by myself and another reviewer, and the manuscript is much improved. I still have some, relatively minor, issues with the manuscript, as detailed below. Once these are addressed I can recommend publication in ACP.

While the claims of “stabilisation”, “promotion”, “enhancement” etc have been toned down, and I especially appreciate the rewriting of the title, there are still a number of sentences that I feel are not really supported by the computed data.

-First, in the last sentence of the abstract, please explicitly spell out the conditions where the claim holds, i.e. replace the last part of the sentence by something like “promotes new particle formation in the atmosphere, at least in conditions where the SUA concentration is significantly larger than the SA concentration”.

We have added a phrase “particularly under polluted conditions with high concentration of diverse organic acids.”

-On line 259, the authors state that the negative hydration free energies suggest that “hydration stabilises the clusters”. This does not really follow, at least not if “stabilisation” is meant to mean stability toward the evaporation of acid or base molecules, not just toward the evaporation of water. Having a strongly negative free energy for the AB + W => ABW reaction may OFTEN correlate with having lower evaporation rates for the hydrated cluster (i.e. ABW => AW + B or ABW => BW may be slower than AB => A + B) but this is not necessarily the case: if the A + W or B + W reactions have even more negative free energies, then hydration will actually INCREASE the evaporation rate of AB, instead of decreasing it. (Examples of this can likely be found even in the authors’ own data. Also note that this applies for any number of A, B & W molecules in the cluster, not only the three-molecule example I discuss above). So, to recap: negative hydration free energies just mean that the cluster likes to be hydrated. It doesn’t in and of itself imply anything about the more general “stability’” of the cluster, and claiming such an implication is incorrect.

We have changed our statement as suggested “Figure 5a shows that the stepwise hydration energies are negative at most hydration degrees, suggesting that hydration is thermodynamically favorable”.

-Line 272: again this “energetically favourable” term: technically true by some definition, but very very misleading when applied to cases where the free energy of the addition reaction is only marginally negative (i.e. not even close to the approximately -10 kcal/mol threshold needed for the evaporation rate not to vastly exceed the formation rate at trace-gas concentrations).

We have removed this statement.

-Line 287: sometimes the described interactions are indeed “synergetic” (should that be “synergistic”?) , but in many cases it seems they seem to rather be “antagonistic”, for example when the presence of SUA actually hinders SA-DMA clustering. This fact, that the multi-component interactions can go “both ways” in terms of their effects of clustering, could be noted here.

We have changed our statement as “It is evident that the Gibbs free energy changes of SUA addition to the multi-component clusters are relevant to the hydration degree and the base types”.

-Line 293-297: here the authors engage in some sort of “bait and switch” argumentation which is frankly quite intellectually dishonest. First they acknowledge that the free energy of adding SA to SA*DMA*SUA is higher than that of SA addition to SA*DMA. And then they state - as if this somehow invalidated the former conclusion - that “the free energies for adding SA to SA*DMA*SUA*(W)x clusters are negative”. Well yes, even the addition of SA to SA*DMA*SUA without water molecules was NEGATIVE - it was just less negative than the competing addition to SA*DMA. The crucial point here is that the SA + SA*DMA*SUA*(W)x reaction free energies (with x = 1…5) are all ONLY VERY SLIGHLY negative - actually even less negative than the x = 0 case. So in other words the SA molecule will very very rapidly evaporate from the (SA)2*DMA*SUA*(W)x clusters. Again, the “energetically favourable” argument made here may be technically true (by some, fairly irrelevant, definition of favourable), but completely and absolutely misleading: the (SA)2*DMA*SUA*(W)x clusters are actually very very unstable with respect to SA loss, and this should be honestly admitted here! We have changed our statements as “With hydration (i.e., $(SA)_2$•DMA•SUA•(W)x), the free energies for adding SA to SA•DMA•SUA•(W)x clusters are negative (Table 2)”. Furthermore, we have added discussions on atmospheric conditions regulating cluster growth or evaporation on p.18 “Clearly, the ability whether a cluster grows to form a nanoparticle is dependent on the competition between the forward reaction by adding a monomer and the backward reaction by losing a monomer (evaporation) at each intermediate step. Hence, the clusters grow (or evaporate) when $k_i^+[A_i]$ is larger (smaller) than k_i^- (eq. 11). While the evaporation rate relies on the thermodynamic stability of the cluster, the forward rate constant is kinetically controlled, dependent on the interaction (i.e., the natural charges and dipole moments) and kinetical energies between the colliding cluster and monomer (Zhang et al., 2012)”.

-There seems to be something wrong with equation 9 or how it is defined: if this the [cluster] variable is supposed to be the absolute concentration a cluster with x SA molecules, y W molecules, z AM molecules, n DMA molecules and m SUA molecules, then the expression should read

[cluster] = [SA]^x[W]^y[AM]^z[DMA]^n[SUA]^m exp(-dG/RT)

If the [cluster] variable is instead some relative concentration measure (as implied in some parts of the text), then this needs to be explained/defined better. Since I don’t understand exactly what the authors are calculating, I can also not evaluate the arguments on lines 349-351, where the computed values are used to support an argument about SUA “likely contributing to further growth” - however given the issue with the discussion on lines 293-297 described above I’m a bit suspicious about this claim too.

Eq. 9 has been modified as “$[cluster] = [SA]^m \times [AM]^n \times [DMA]^l \times [SUA]^k \times e^{\left(\frac{-\Delta G}{RT}\right)}$ (9) where ΔG corresponds to the Gibbs free energy change for the reaction: mSA + nAM + lDMA + kSUA→ $(SA)_m$•$(AM)_n$•$(DMA)_l$•$(SUA)_k$”.

-The Ho et al reference seems to be about the urban atmosphere in China - this is unlikely to be

representative of global dicarboxylic acid concentrations (which are very likely lower). It may well be that such global estimates do not exist - but then the authors should openly admit this, and also acknowledge that the SUA concentrations that they use likely correspond to the upper end of the global range. (This will require some amendments to the discussion on page 17 - also the use of the phrase “typical abundances” on page 19 is not really justified).
We have added statements in Conclusion part p.19-20 “Various organic acids are produced from atmospheric oxidation of volatile organic compounds (VOCs) from biogenic (i.e., pinenes) and anthropogenic sources (i.e., aromatics). Our results indicate that the multi-component molecular interaction involving organic acids, sulfuric acid, and base species promotes NPF in the atmosphere, particularly under polluted environments. The role of different organic acids with distinct functionality in NPF needs to be further assessed. In particular, future studies are necessary to evaluate both the kinetics and thermodynamics of the interactions of organic acids with SA and base species, i.e., the forward and reverse rates as well as the potential energy surfaces for cluster formation, in order to develop physically-based parameterizations of NPF in atmospheric models”.

-The authors suggest on line 379 that “the presence of organic acids typically increases the dipole moments of clusters”. This may be generally true, however for comparing the competing mechanisms SA*DMA and SA*DMA*SUA, it’s not clear that the SUA-containing clusters will have necessarily have higher dipole moments than the corresponding SUA-free clusters. Since the authors actually have a huge amount of cluster data (including dipole moments) perhaps they could present the dipole moments for all the clusters in Table 2, to see if the argument actually holds for the specific systems studied here?
We have added the dipole moment data in Table 6. In addition, we have added a sentence on p. 17 “Furthermore, the dipole moments of SA•DMA•SUA and SA•AM•SUA are 7.4559 and 8.7764, respectively (Table 6), which are the largest among those of the trimers”.

-On line 380, the authors again use the (often only very slightly) negative addition energies to imply that “SUA likely stabilises the SA*base clusters”. This is problematic in two ways: first, as discussed above, the authors own data indicates that for example the (SA)2*DMA*SUA*(W)x will actually lose SA very rapidly, and second, as discussed above in the context of hydration, even a strongly negative free energy for e.g. AB + SUA => (A)(B)(SUA) does not necessarily mean that the loss rate of A or B is decreased - it can even increase, if the binding of SUA to A or B individually is even stronger. I suggest just removing this whole sentence.
We have removed the sentence as suggested.

-Analogous to the introduction, please specify also in the conclusion that the “promoting” effect the authors claim to have discovered (which I am overall very sceptical about overall given the very high SA loss rates from the only SUA-containing 2-SA clusters studied in the paper) is only important when the SA concentration is relatively low, AND the SUA concentration high (i.e. it’s not enough for the conditions to just be “polluted”, they have to be “polluted” in a very particular way).
We have added statements in Conclusion part “Various organic acids are produced from atmospheric oxidation of volatile organic compounds (VOCs) from biogenic (i.e., pinenes) and anthropogenic sources (i.e., aromatics). Our results indicate that the multi-component molecular

interaction involving organic acids, sulfuric acid, and base species promotes NPF in the atmosphere, particularly under polluted environments”.

Meanwhile, we have added a phrase in the abstract “particularly under polluted conditions with high concentration of diverse organic acids”.

-The Kurtén et al 2008 paper (which by the way seems to be missing from the reference list even though it’s cited) is not a good primary reference for atmospheric DMA concentrations (it’s a purely computational study).
We have removed the citation “Kurtén et al 2008” and added a reference to the atmospheric DMA concentrations in Table 3 “[c]Ge et al. (2011).”