

Interactive comment on “Interaction between Dicarboxylic Acid and Sulfuric Acid-Base Clusters Enhances New Particle Formation” by Yun Lin et al.

Anonymous Referee #1

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Yun Lin and co-workers have used computational methods to study clusters containing sulfuric acid (SA), ammonia (AM), dimethylamine (DMA), succinic acid (SUA) and water. The computational methods used are adequate for the purpose (if a bit outdated in terms of the DFT method used to obtain the thermodynamics - the sampling approach on the other hand is state-of-the-art). The purpose of the study is to assess the possible atmospheric significance of succinic acid in promoting sulfuric acid-based new-particle formation (and indeed a positive conclusion is implied even in the title). The study provides important new insights and information onto e.g. the hydration behaviour of SA-AM-DMA-SUA clusters, and especially on how this changes with the presence of SUA. Some of the conclusions concerning the effect (or lack of

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effect) of SUA on new-particle formation are somewhat premature, and not always fully supported (indeed, sometimes flat-out contradicted) by the actual data. While the manuscript is publishable, extensive rewriting and reformulation is thus necessary prior to publication in ACP.

Major comments:

1) Overall, the authors attach way too much importance to the sign of the standard Gibbs free energy change, “delta-G”. (This is unfortunately very common in similar studies.) The free energies are computed using a 1 atm reference pressure (values computed with other reference pressures would be very different for reactions where the number of molecules changes, as in all the clustering reactions studied here). The concentrations of the studied reactants are (except for water), far far below 1 atm, as the authors themselves note. In other words, the reference pressure is essentially (for these reactions) an arbitrary value that has very little to do with the particular reactions being studied. A negative “delta-G” value for a clustering reaction is a necessary, but very far from sufficient, criterion for the cluster to be said to be “stable”. Consider for example a reaction of the type $X + Y \rightleftharpoons XY$ where X is some core cluster, and Y is a molecule present at ppt - levels (i.e. a partial pressure of $1E-12$ atm, typical for e.g. SA, DMA or SUA in this study). If the delta-G for this reaction is for example -3 kcal/mol, we can use the law of mass balance to write (here R is the gas constant, $T=298K$ is the temperature, e.g. p_{XY} is the partial pressure of XY, and p_{ref} is the reference pressure at which delta-G is computed, in this study 1 atm):

$$(p_{XY}/p_{ref}) / ((p_X/p_{ref})(p_Y/p_{ref})) = \exp(-\Delta G/RT)$$

We can solve for the ratio (p_{XY}/p_X) , and get $(p_Y/p_{ref}) \exp(-\Delta G/RT)$

Since p_Y/p_{ref} is $1E-12$, and $\exp(-\Delta G/RT)$ is (for a delta-G of about -3 kcal/mol) about 160, we get a value of about $1.6E-10$ for the ratio. In other words less than one in a billion of the molecules of type Y will be bound to XY clusters at equilibrium, despite a negative delta-G value. Clearly, XY is not “stable” in any meaningful sense of the word,

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and Y does not “stabilise” X, despite the standard free energy of addition of Y to X being negative. Thus, sentences such as (line 285-286) “All free energy changes shown in Figure 5b are negative, confirming that SUA stabilizes the SA base clusters” are absolutely false: negative free energy changes do not in any way confirm “stabilisation”. (Also, even when a molecule Y is very strongly bound to a cluster X, this does not in and of itself prove “stabilisation” of the cluster as a whole: it just proves that it is difficult for molecule Y to evaporate. Other constituents of the cluster may evaporate either more or less easily due to the presence of Y, and this needs to be separately evaluated - just looking at the Y to X binding is not sufficient to claim “stabilization”).) I recommend that the authors search the manuscript for all occurrences of the word “stable” in any form (verb or adjective), and rigorously consider whether or not its use is justified. My guess is that almost none of the claims of “stability” or “stabilisation” are actually really justified (apart from perhaps the discussion on hydration, where the effect of H₂O concentration is properly accounted for) - the binding of SUA to the clusters tends to be quite weak, with the equilibrium strongly on the side of the reactants even for the highest SUA concentrations claimed by the authors. (See Elm et al., 2017, also cited in the manuscript, for a discussion on what is actually required for a cluster to be “stable” given trace-gas concentration levels of the constituent monomers: this typically means delta-G values far below -10 kcal/mol - which is not reached for any of the SUA addition steps in the manuscript.)

2) Related to the previous point, the most interesting part of the data in terms of evaluating the role of SUA on new-particle formation are the energetics for the formation of the clusters shown in Figure 8, i.e. the clusters with two SA molecules. From table 2, it seems that the SA addition free energies to the (SA)(SUA)(DMA)(W)_n clusters vary between +2 and -6 kcal/mol, with the value for the unhydrated cluster being -5.14 kcal/mol. This is significantly HIGHER (more positive) than the free energies of SA addition to the (SA)(DMA) cluster or the (SA)₂DMA cluster (without any SUA), which are about -18 and -9 kcal/mol (respectively) according to the coupled-cluster (DLPNO-CCSD(T)) study of Myllys et al <https://pubs.acs.org/doi/suppl/10.1021/acs.jpca.5b09762>), and even more

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negative according to older DFT - or RICC2- based - studies. (In the absence of data at the exact level used by the authors of this study a direct comparison is impossible - the authors might want to compute at least the unhydrated SA(2)DMA and possibly (SA)3DMA clusters just to check.) Thus, the data presented here indicates - in direct contrast to the manuscript title - that the presence of SUA actually HINDERS sulfuric acid - DMA nucleation rather than enhancing it. I strongly urge the authors to reformulate their title in light of this observation (as well as the comments on stability presented above). Also claims such as SUA “promoting subsequent growth” seem unlikely to be true, if the net effect of SUA is to decrease rather than increase the uptake of further SA molecules.

3)The authors present somewhat misleading concentration ranges and ratios for SUA and SA. The SA value of $1E5$ molecules per cm^3 corresponds to fairly clean conditions - in polluted environments the SA concentration can easily be a couple orders of magnitude higher. The SUA concentration of $1E7$ quoted is from Los Angeles, which I presume corresponds to fairly polluted conditions (with SA certainly exceeding $1E5!$) - in clean conditions the SUA concentration is very likely much lower. The total organic acid concentration range of $1E8$. . $1E9$ quoted is valid, BUT the majority of these will be simple monocarboxylic acids - dicarboxylics such as SUA will only account for a small fraction of the total. Thus, the $[SUA]/[SA]$ range used in the paper (1 to 10 000) is obtained by combining minimum values for SA with maximum values for SUA - in reality, the ratio may well be below one in most places, and I find it hard to believe that values of 10 000 will be found anywhere in the atmosphere. Using the range 1 to 10 000 is fine for answering the question “could SUA possibly play a role in NPF anywhere in the atmosphere, even in the best case”, but then this should be stated openly, instead of implying that the range used is representative for most areas of the world. Again, together with the two previous issues, this indicates that the statement in the manuscript title is exaggerated at best, and false at worst.

Minor comments:

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-In the BPMC conformational sampling, what force field was used for the SA, AM, DMA and SUA molecules? (For water TIP3P was apparently used.) Presumably some variant of the AMBER force field, but this should be stated.

-In reaction equations (e.g. 4, 5), arrows (going in both directions to indicate a reversible reaction) should be used rather than equals signs

-On line 218, please specify that the proton transfer occurring upon hydration of (SA)(AM)(DMA)(W5) is the SECOND proton transfer, forming the sulfate dianion (overall, it would be good to separate discussion of first and second proton transfers).

-It's a bit unclear what's being plotted in Figure 5a, apparently the free energy of the reaction $X + nH_2O \Rightarrow X(H_2O)_n$ where X is some core cluster? This could be explicitly specified. Or even better, plot the stepwise hydration energies instead, as the actual hydration in the atmosphere likely involves addition (or removal) of single water molecules, not e.g. 5 molecules at the same time. (Since the stepwise energies are then referred to in discussing the hydrate equilibria, it would be better to plot them in the first place.)

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