Reply to comments on "Insights into the role of dicarboxylic acid on CCN activity: implications for surface tension and phase state effects" by Xiong et al.

Reply to Anonymous Referee #2

1) The manuscript by Xiong et al. discussed the impact of surface tension reduction on CCN activity of dicarboxylic acid-inorganic salt mixtures. CCN activity was quantified using the CCN counter, and surface tension was measured using the AFM. The data suggested that observed kappa values for adipic acid (AA) and octanedioic acid (OA) cannot be well explained by chemical composition when surface tension of water is assumed. The AFM data demonstrated that the values of surface tension for these particles were significantly lower than that of water. The result makes sense, and the output of the study will be useful for future studies on CCN activity. I have some comments on the manuscript that needs to be considered for making it to be acceptable to the journal. I also suggest the authors to ask a native speaker of English for checking grammatical issues on the manuscript.

Response: We truly appreciate the constructive comments and suggestions raised by the reviewer. Those comments are valuable and very helpful for improving our paper, as well as the important guiding significance to our studies. Below we provide a point-by-point response to individual comment. The responses are shown in brown and bold fonts, and the added/rewritten parts are presented in blue and

bold fonts. Also, we have asked native speaker of English for checking grammatical issues and the revised manuscript has been improved.

Major comments:

2) The manuscript qualitatively connected reduction in surface tension and kappa. However, these two parameters are not quantitatively connected in the current manuscript. For instance, it would be possible to develop a multicomponent Kohler model considering water-solubility of pure organic compounds, and investigate sensitivity of the measured kappa values on the assumed value of surface tension. If the measured values of surface tension can explain the experimentally constrained value of kappa, this study could be more quantitative. The reviewer would imagine that the quantitative study could have been easier if information about particle water contents were to be available for the AFM data. Would the authors provide comment on it?

Response: Thank you for the suggestion. Actually, we could not obtain water content from AFM data. But it is a very good idea to constrain the water solubility and surface tension in Köhler model. Here, we used the solubility-involved Köhler model which was introduced by Petters and Kreidenweis (2008), to investigate sensitivity of the measured κ_{CCN} values on the assumed value of surface tension for inorganic salts/OA systems (results for inorganic salts/AA were not shown here because there were only two measured surface tension results).

As shown in Figure 1a, κ_{CCN} of NaCl/OA with 60%, 75% and 89% OVF derived from solubility-involved Köhler model (circles) with water surface tension were 0.515, 0.324 and 0.145. These values underpredict our κ_{CCN} base on CCN measurement (0.688, 0.485 and 0.296, triangles). However, if modeled κ_{CCN} values fit the measured

values, the corresponding surface tensions should reduce to 65.4 mN m^{-1} (60% OVF), 62.7 mN m^{-1} (75% OVF), 56.7 mN m^{-1} (89% OVF). Similar results were also found for AS/OA systems (Fig.1b).

In Fig. 1c, fitted surface tension showed good linear relation with measured surface tensions (slope and R^2 is 1.01 and 0.71, respectively.). This could provide a quantitate way to predict κ_{CCN} values of inorganic salts/OA by solubility-involved Köhler model, by using their measured surface tensions results.
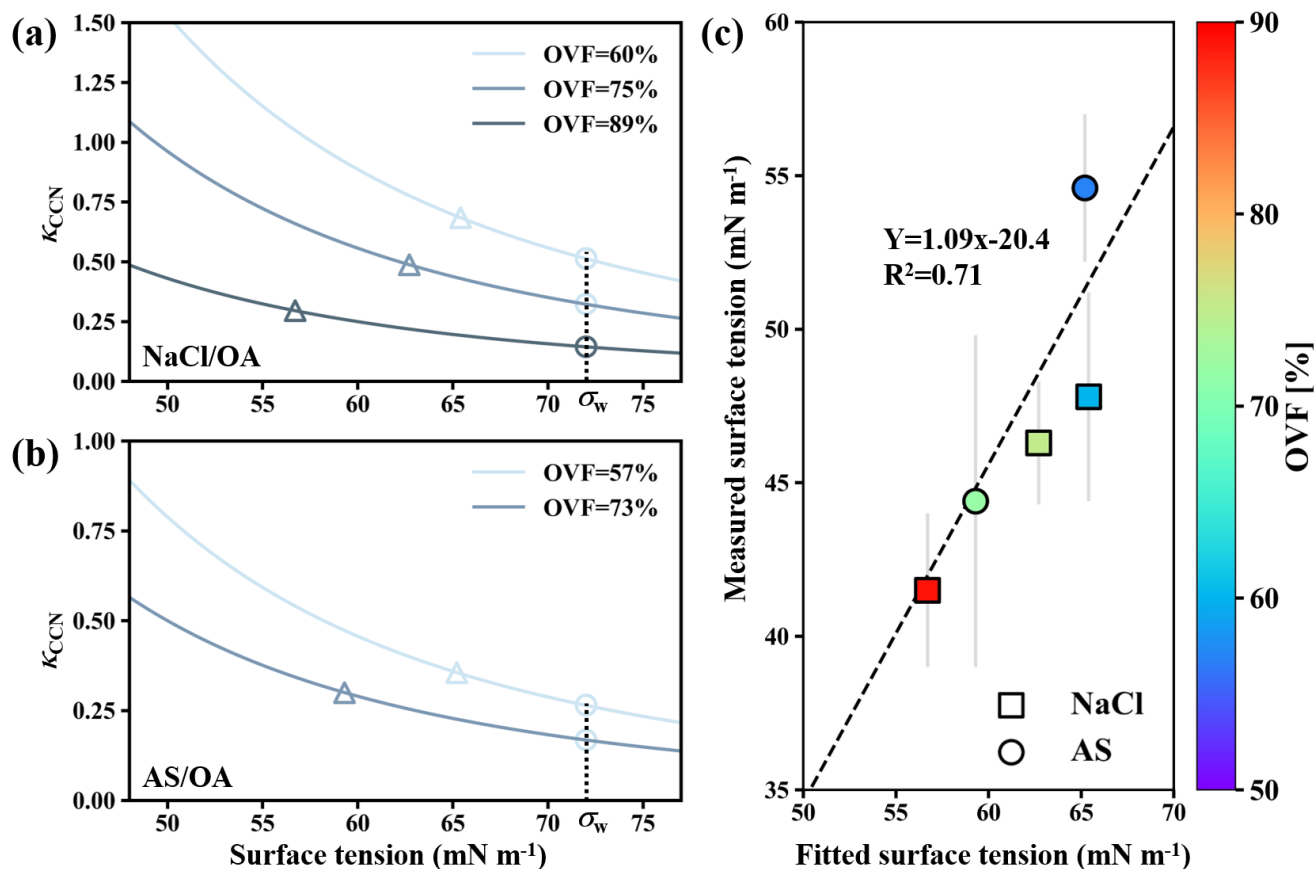
Fig. 1 κ_{CCN} vs. assumed surface tension for (a) NaCl/OA and (b) AS/OA systems according to solubility-involved Köhler model presented by Petters and Kreidenweis (2008). The triangles and circles in (a) and (b) represent the measured κ_{CCN} and predict κ_{CCN} by solubility-involved Köhler model. Closure between

fitted surface tensions and measured surface tensions (c). σ_w represents water surface tension (72 mN m^{-1}).

Minor comments:

1) **Title:** Researchers in the area already know that dicarboxylic acids are important contributors to CCN. It is better to stress the novelty of the study in the title better.

Response: Thank you for the suggestion. We have revised our title.

Revision/addition:

Title: "Reconsideration of surface tension and phase state effects on CCN activity based on the AFM measurement."

2) **Line 36**: Add references to support the statement.

Response: Thanks, we have added references.

Revision/addition:

Line 37: The role of particle chemistry in the activation process, however, is still debatable due to the complexity of chemical constitution (Bhattu and Tripathi, 2015; Noziere, 2016).

3) **Section 2.1.2**: qualities of the compressed air and water for the atomizer are very important for CCN activity studies of acidic chemical species. Ammonia ubiquitously exists in an indoor environment. Based on the reviewer's experience, it has never been easy to generate ammonia-free dicarboxylic acid particles. I suggest adding further details about particle generation in the revised manuscript.

Response: Thank you for the advice. We have added the details of water information in section 2.1.2. For the indoor ammonia, we agree the possible influence of indoor ammonia during the generation of acid particles. But the consistence of κ_{CCN} between our results and previous studies (e.g. malonic acid, succinic acid and adipic acid) implied that this influence might be ignored.

Revision/addition:

Line 82: In brief, particles containing single and mixed chemicals were generated by clean and particle-free compressed air with water solutions (~ 1‰) by a constant output atomizer (TSI 3079A). The solutions were prepared by using ultrapure water (Millipore, resistivity ≤ 18.2MΩ).

4) **Line 93:** Is there any reason why the authors selected the hydrophobic silicon wafer as a substrate? What would be the advantages/disadvantages of the substrate when compared with other types of substrate?

Response: The hydrophobic silicon wafer was frequently used to measure single particle's surface tension using AFM (Morris et al., 2015; Lee et al., 2017; Lee et al., 2020). The different types of substrate results in different affinity between water and substrate. Hydrophobic silicon wafer used in our study has been proved that almost all of the solute can be collected into the solute aggregate on the surface after water evaporation (Ding et al., 2020). Therefore, our hydrophobic silicon wafer removes the possible loss of solute when RH varies (especially RH decreases), which could not be ensured by other types of substrate such as commonly used mica sheet and normal silicon wafer with no hydrophobic coatings on surface.

Revision/addition:

Line 97: "**particle sizing sampler (Models BGI20800 Series, BGI Incorporation) onto hydrophobically silicon wafers.** The hydrophobically silicon wafers are with polydimethylsiloxane brush surface, so solute can be collected into the solute aggregate on the surface after water evaporation when RH varies (especially RH decreases) (Ding et al., 2020)."

5) **Line 99:** I checked the datasheet of SHT 85. The accuracy of the sensor is +-1.5%. The authors mentioned in the manuscript that the AFM measurement was conducted at 99.5% of RH. The uncertainty of 1.5% for the high RH region influences significantly influences thermodynamic properties. The potential influence of uncertainties in RH measurements on the AFM data would need to be discussed in detail.

Response: Thank you for the comment. We agree that under such high RH level, ± 1.5% accuracy may bring uncertainties in droplet water content and surface tension results. Therefore, we successively obtained more than 10 force plots of at least 5 individual droplets in within 5~10 minutes to decreased the uncertainties as much as possible. In our study, most of the results (97%) showed standard deviation within 10%, showing a relative low effect on surface tension results. Especially for inorganic salts mixed with MA, PhMA, SA, PhSA and PA, their standard deviations are even lower than 6%, indicating a negligible influence of RH sensor accuracy in this study.

Revision/addition:

Line 104: "was achieved and maintained by humidified flow. RH in cell was measured by a RH sensor (SHT 85, ± 1.5% uncertainty, Sensirion Inc.)."

Line 116: "More than 10 force plots were collected on at least 5 individual droplets in order to decreased the uncertainties (e.g. sensor accuracy)".

6) **Line 103:** Ideally, this manuscript should be published after the publication of the procedure for making the nanotip. At least, the name of the potential first author needs to be stated so that the readers will be able to search for the corresponding paper if necessary.

Response: Thank you for reminding. The manuscript about making nanoneedle has been published and the reference has been added in the revised manuscript.

Revision/addition:

Line 107: "… The procedures of making nanotips were detailly described in Ding et al. (2022) and a brief description was given here.

7) **Line 122:** OVF needs to be defined.

Response: The definition has of OVF has been added.

Revision/addition:

Line 132: OVF indicates the organic volume fraction of mixed particles.

8) **Line 133:** Although the authors mention that the data are consistent with previous results, they are actually slightly different, as discussed in the following sentences in the same paragraph. The expression should be updated for representing the comparison more accurately.

Response: We have added more descriptions about the comparison as suggested.

Revision/addition:

Line 141: "κ_{CCN} values for single component aerosols were summarized in Table 2. κ_{CCN} of NaCl, AS, MA, SA and AA were 1.325 ± 0.038, 0.562 ± 0.059, 0.240 ± 0.036, 0.204 ± 0.023 and 0.008 ± 0.001, respectively, being **overall** consistent with previous results (Petters and Kreidenweis, 2007; Kuwata et al., 2013). **κ_{CCN} of NaCl and MA were slightly higher while AS was slightly lower than those reported in Petters and Kreidenweis (2007). This may be ascribed to the solute purity (Hings et al., 2008). Based on the same reason, κ_{CCN} of PA (0.112 ± 0.010) and OA (0.003 ± 0.0002) were 20% lower and twice higher than those reported by Kuwata et al. (2013), respectively.**"

9) **Line 144:** It is not clear to me how the criteria for highly- and slightly- soluble compounds were developed, and why it is important for the present study. Further information is needed.

Response: Sorry for the misunderstanding. The criteria for highly and slightly soluble compounds was set to 100 g/ L according to Kuwata et al. (2013) and Luo et al. (2020). The κ_{CCN} values for highly soluble components (MA, PhMA and PhSA) displayed no monotone trend with solubilities, while κ_{CCN} values of sparely soluble components (AA, PA, SA and OA) showed an increased trend with solubility.

Revision/addition:

Line 148: "Solubility and molar volume of dicarboxylic acids were essential factors influencing their hygroscopicity (Kumar et al., 2003; Han et al., 2022). **Therefore, solubility criteria of 100 g/L was used in our study to distinguish the effect of**

solubility of highly soluble (with water solubility over 100 g L^{-1}) and slightly soluble organics (with water solubility below 100 g L^{-1}) on their hygroscopicity, according to Kuwata et al. (2013) and Luo et al. (2020)."

10) **Line 172-174:** I could not understand what this long sentence means well. It would be great if the authors could update the description.

Response: We are sorry for misunderstanding, we have revised the description.

Revision/addition:

Line 182: "Thus, addition of inorganic salts facilitates deliquescence of OA and AA under lower RH, further promotes their phase state transition from solid to liquid (or semisolid), and their surface tension would be reduced. Based on surface tension results of water solutions, Aumann et al. (2010) reported that surface activities of dicarboxylic acids were increased with their carbon number. Therefore, surface tensions of inorganic salts/AA and inorganic salts/OA may decrease more than the rest acids containing particles, resulting in their relatively higher κ_{CCN}. This indication was further confirmed by AFM surface tension measurement, as discussed in Section 3.4."

11) **Table 1:** What does 'guaranteed reagent' mean? Would you provide the detailed information about what is specifically guaranteed?

Response: Detailed information has been provided.

Revision/addition:

Compounds	Molar weight (g mol^{-1})	Density (g cm^{-3})	Solubility (g L^{-1})	DRH (%RH)	Purity	Supplier

NaCl	58.44[a]	2.16[a]	360[b]	73-77[c]	**≥99.8%**	Sinopharm Chemical Reagent
AS	132.13[a]	1.77[a]	770[b]	78-82[c]	≥99%	Sigma Aldrich
MA	104.06[a]	1.63[a]	1400[b]	65-76[c]	≥99%	Sigma Aldrich
PhMA	180.16[a]	1.40[a]	131[a]	NA	98%	Aladdin
SA	118.09[a]	1.57[a]	80[b]	98[d]	≥99%	Aladdin
PhSA	194.19[a]	1.13[a]	241[a]	NA	98%	Macklin
AA	146.14[a]	1.36[a]	14.4[b]	∼100[e]	**≥99.8%**	Sinopharm Chemical Reagent
PA	160.17[a]	1.28[a]	25[b]	>90[c]	99%	Macklin
OA	174.20[a]	1.16[a]	12[a]	>90[c]	99%	Aladdin

12) **Table 2:** Please use "Not Available" when a previous study does not exist, rather than mentioning 'this study.'

Response: We have revised Table 2

Revision/addition:

Chemicals	D_d (nm)	κ_{CCN} mean ± standard deviation	Previous reported κ_{CCN}
NaCl	50, 65, 76, 88, 100	1.325 ± 0.038	1.28[a]
AS	50, 65, 76, 88, 100	0.562 ± 0.059	0.61[a]
MA	50, 65, 76, 88, 100	0.240 ± 0.036	0.227[a]
PhMA	50, 65, 76, 88, 100	0.183 ± 0.032	**NA**
SA	50, 65, 76, 88, 100	0.204 ± 0.023	0.166-0.295[a]
PhSA	50, 65, 76, 88, 100	0.145 ± 0.017	**NA**
AA	140, 160, 180, 200	0.008 ± 0.001	0.005-0.008[b]
PA	65, 76, 88, 100	0.112 ± 0.010	0.14[b]

OA	200, 220, 240, 260	0.003 ± 0.0002	0.001^{b}

[a] Petters et al., 2007; [b] Kuwata et al. (2013) and references therein; **NA indicates no reported results are available.**

Reference

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