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 #1

1) This manuscript investigated the CCN activity of the mixtures of inorganic salt and dicarboxylic acid and further determined their phase state and surface tension by using the atomic force microscopy. The results show that the bias between the κ_{CCN} and κ_{Chem} of inorganic salt/AA and inorganic salt/OA can be explained by the surface tension reduction. The study highlights the role of surface tension reduction in evaluating CCN activity. The study is interesting in several aspects. The topic is one that is currently undergoing debate in the atmospheric chemistry and aerosols science communities, and it is of interest to the readership of ACP. The study could be acceptable for publication if revisions are made with consideration of the issues listed below.

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.

Major comments:

2) One of my major concern is that the measured size of collected particles in this study, which ranged from 0.4-1μm. But, as has been known that, surface tension lowering effect by the surfactants was more important or obvious for fine and ultrafine particles with diameters smaller than 100 nm (Ovadnevaite et al., 2017). As particles grows, the solution is diluted and the surface tension lowering effect becomes weak. So, it would be more meaningful and or with scientific significance if the authors could look at and measure the smaller size particles.

Response: Thank you for the advice. We totally agree that the surface tension effect of surfactants on hygroscopicity and CCN activity is more important with respect to smaller particles. However, it still remained a big challenge for directly obtaining surface tension of submicron particles. To our knowledge, there is no reported results that obtained surface tension of particles with diameter smaller than 100 nm. The size of collected particles for surface tension measurement using AFM are usually ranged in 0.5-1μm (Morris et al., 2015; Lee et al., 2017), which is limited by the diameter of nanoneedles. The diameter of High Aspect Ratio (HAR) nanoneedles should be smaller than 50 nm to detect surface tension of 100 nm particles. In our study, we used focused ion beam (FIB) induced deposition to produce needles with constant diameter (Ding et al., 2022). This method is difficult to make nanoneedles with diameter smaller than 100 nm. We are trying to improve our method in making AFM probe to measure the surface tension of smaller particles in the future.

2) Moreover, in this study, the κ closure was conducted by measuring the pure and mixed inorganics and organics. However, the authors measured within the size range of ~50-260 nm as given in Table 2, which is different with the size range when they used for measuring surface tension. So, can the bias between κ_{CCN} and κ_{Chem} based on the larger size explain the effect of surface tension reduction? The surface tension should also dependent on particle size.

Response: Thank you for the comment. We agree that the surface tension is dependent on particles size. Indeed, we admit that the discrepancy of particle diameter between surface tension and CCN activity experiments. However, we think this is not the main reason to explain the bias between κ_{CCN} and κ_{Chem}.

1) As demonstrated by Cheng et al. (2015), the size dependence of interfacial energy will not play a significant role unless the solution droplets are smaller than 5 to 6 nm. Thus, the discrepancy of particle diameter between CCN experiment and AFM measurement may not affect our results.

2) Small droplet presents a higher surface-to-volume ratio than that of large particle (Ruehl and Wilson, 2014). Sorjamaa et al. (2004) and Miles et al. (2019) demonstrated that larger fraction of surface-active molecules in the small droplet may partition to the surface and surface tension reduction in small droplet possibly be stronger than large droplet.

Revision/addition:

1) Part of section 2.1.3, L119: "…**However, it should be noted that the potential uncertainty introduced due to the different particle diameter in CCN activity (ranged in 50~260 nm) and AFM experiments (0.4-1μm) is not taken into account, because**

the size dependence of surface tension is not significant unless the solution droplets are smaller down to 6 nm (Cheng et al., 2015)."

3) In addition, it is not very clear that how did the author get the κ values of each individual pure component, some more details are suggested to include in the Method.

Response: Thank you for the suggestion. We have added the corresponding descriptions in Section 2.2.

Revision/addition:

Part of section 2.2, L124: "Based on κ-Köhler theory, hygroscopicity parameter κ_{CCN} **for individual pure component and mixed aerosol** can be calculated by:

$$\kappa_{\mathrm{CCN}} = \frac{4A^3}{27D_d^3 ln^2(1+s_c)}, A = \frac{4M_w\sigma_w}{RT\rho_w} \qquad (1)$$

where σ_{w}, M_{w} and ρ_{w} are surface tension, molecular weight and density of water, respectively. R is universal gas constant and T is temperature (298.15K). s_{c} is critical supersaturation ratio. D_{d} is dry diameter. In addition, hygroscopicity κ of multicomponent chemical system can also be calculated assuming a Zdanovskii, Stokes, and Robinson (ZSR) simple mixing rule. κ based on the chemical composition (κ_{Chem}) of mixed aerosol was calculated by:

$$\boldsymbol{\kappa_{\mathrm{Chem}} = OVF \cdot \kappa_{\mathrm{org,CCN}} + (1 - OVF) \cdot \kappa_{\mathrm{inorg,CCN}}} \;, \qquad (2)$$

where $\kappa_{\mathrm{org,\ CCN}}$ and $\kappa_{\mathrm{inorg,\ CCN}}$ are obtained κ_{CCN} values of single organic acid and inorganic salt."

4) Also, it is mentioned in the paper that the surface tension lowering is jointly determined by solubility, deliquescence RH and surface activity, and the influence of

solubility is greater. This conclusion is based on the data results that the surface tension of the two dicarboxylic acids (AA and OA) with low solubility decreases significantly at most. At the same time, these two dicarboxylic acids also have the higher deliquescence point and the longer carbon chain. However, the influence of deliquescence point on surface tension has not been discussed in this paper. As mentioned earlier, the particles are already liquid when measuring, that is, fully deliquescence. Is there a causal relationship between the deliquescence point and the surface tension lowering? In addition, does the carbon chain length mean that the surface activity must be strong? The authors may refer some previous studies to further clarify this.

Response: Sorry for the misunderstanding.

1) We have realized that it is inappropriate to indicate the relation between surface activity and deliquescence RH based on our results. Therefore, we have removed the corresponding descriptions.

2) We have added the corresponding references to demonstrate that the surface activity of dicarboxylic acid become strong with increased carbon number.

Revision/addition:

Part of Section 3.4.2, L267: "…Besides, notable surface tension reductions of particles containing OA or AA indicated that organic solubility plays an important role in surface tension reduction as AA and OA have the lowest solubilities among studied dicarboxylic acids. **OA and AA own higher carbon numbers than most of the rest studied organics. Since Aumann et al. (2010) found that the surface activity of dicarboxylic acids increases with carbon number from 2 to 9 based on surface tension measurement of their water solutions, indicating that dicarboxylic acids (e.g. OA and AA) with higher carbon number own stronger surface activity. Therefore, strong**

surface activity of dicarboxylic acid is another factor attributing to surface tension reduction of inorganic salts/dicarboxylic acids."

Conclusion:

1) L286: "…**Slightly dissolved dicarboxylic acids with lower solubilities and strong surface activity are more likely to cause notable surface tension depression for inorganic salt/dicarboxylic acid mix particles.**"

2) L289: "**…especially for slightly soluble organics with lower solubilities and strong surface activity.**"

References

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