

Interactive comment on “Joint effect of organic acids and inorganic salts on cloud droplet activation” by M. Frosch et al.

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Anonymous Referee #2

We thank the referee for the constructive comments on our manuscript. We have addressed all comments in a point by point fashion below. During revisions we realized that there was a mistake in our parameterizations of water activity and surface tension as functions of growth factor for pure oxalic acid and its mixtures, partly due to crystal water of oxalic acid. This has been corrected in the text and figures of the revised manuscript. In addition to the comments given by the referees we have im-

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proved/corrected the text in a few other places, reduced the number of significant figures given in Table 6 and changed Fig. 7 so that we now show Köhler curves for dry particle diameter of 35 and 100 nm and also include experimental values for comparison.

“The authors explore the CCN properties of internally mixed particles composed of organic acids and inorganic salts. The authors report surface tension, water activity, and CCN thermo-physical properties for mixed atomized solutions. The phenomenon of solute surface partitioning is not accounted for, but may be observed in the reported measurements. The authors apply Köhler Theory models that include water activity and surface tension values. The models occasionally work well but cannot be applied to all cases. This suggests that solubility and surfactant partitioning are indeed important and must be considered for robust predictions of CCN activity. The subject matter is relevant and of interest to the larger scientific community. The measurements are novel and will add to the existing body of work on model atmospheric aerosol and their subsequent influence on CCN. The manuscript is clear and well written but some references are neglected. The following major and minor concerns address issues that once resolved will clarify key points in the paper.”

“MAJOR CONCERNS The use of the term growth factor, GF, is somewhat unconventional and confusing. Growth factors are commonly provided for a given relative humidity (typically sub-saturated). For CCN measurements, in the supersaturated regime, GF is inconsequential once a critical wet diameter has been achieved; by CCN definition, the droplet will experience uncontrolled rapid growth beyond that point. The authors should emphasize that this study focuses on the processes that lead to CCN activation.”

Page 17987, line 9: The following text has been inserted: “up to the point of activation”

“As such, it is important for the reader to know the GF at activation. What is this value? Is it greater or less than 12 (most of the GF related graphs end at this value)? The

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authors can calculate this value from their CCN measurements. If the GF at activation is considerably small, it will completely change the perspective of the analysis. That is if the value of GF at activation is near 3 then all compounds will significantly affect water activity and must be accounted for.”

Page 17988, line 7: The following text has been inserted: “In this study, critical supersaturations have been determined for internally mixed particles with diameter between 30 and 100 nm. The growth factors at activation of these particles are in the range 3-12.” Furthermore, a new table (Table 7) has been created which links the growth factor at activation with the dry particle diameter and critical diameter.

“P17990 L21. “Neglecting the effects of surfactant partitioning, this means that for example at GF=6 the surface tension of a pure cis-pinonic acid droplet is 59 mNm⁻¹ where as it is 62.06 m M⁻¹ for a droplet solution of the same size formed on a mixed particle”. Isn’t this evidence for strong partitioning effects? That is in the latter case where a 50:50 organic inorganic mixture produces 62 mNm⁻¹ surface tension depression, no surfactant partitioning would result in a higher measured value. Assuming the interactions of ammonium sulfate with water are 72 mNm⁻¹ (in actuality it is a little bit larger) than the mixture where partitioning is negligible should be roughly $65.5 = (72 - 59)/2 + 59$ not 62.06. From the onset of results, it appears that surfactant partitioning cannot be ignored.”

If surfactant partitioning in the bulk solution is important this should be clearly visible in Figure 2a, where the mixed solutions are compared to solutions containing only cis-pinonic acid. Since this is not the case, we have chosen to ignore surfactant partitioning in bulk model solutions, and only mention it in relation to CCN activation.

“The authors should emphasize their key finding that bulk measurements cannot define the nano-scale complexities of CCN activation and growth.”

Page 17988, line 7: The following text has been inserted: “It must be stressed that the physical characteristics measured in bulk solutions may not mirror the physical

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processes and properties of an activating nano-particle.”

“The authors provide very good experimental water activity and surface tension data. These measurements are difficult and provide valuable information yet the models do not capture the aerosolwater dynamics. There are subversive elements that may be unknown and that must be accounted for. For example, surfactant partitioning, water activity (or even both) maybe influenced by dissolution kinetics (Asa-Awuku et al, 2007). The difficulty of the reported measurements and lack of congruency with models should be emphasized in the text. The bodies of work that explore solute partitioning, surface tension, and waters activity are becoming more prevalent in the literature. It is important to acknowledge them so a more complete picture of the nature of the inorganic/organic interactions for CCN properties are elucidated. Below are additional references and discussion topics that are of relevance to this published work.

Asa-Awuku et al., 2008 (salting-out effects of HULIS and ammonium sulphate) Beaver et al., 2010 (surfactant partitioning and the effect of salts) Broekhuizen et al, 2004 (solubility and surface tension properties of model CCN) Fors et al, 2010 (surface tension of HULIS from Biomass Burning samples) Koehler et al. 2006 (Water activity and activation diameters from hygroscopicity or model compounds) Mikhailov et al., 2010 (oxalic acid morphology effects on hygroscopicity and wateradsorption) Padró et al, 2007 (solubility and surface tension properties of model CCN) Wex et al., 2008 (the effects of surfactant partitioning) Wex et al., 2007 (density-ion coefficient and impact on CCN activation)”

We thank the referee for these references which we have included in the text and reference list.

“MINOR CONCERNS

P17983 L22. “Inorganic salts have only a small effect on surface tension in aqueous solution.”. Isn’t this only true if no other compounds are present?”

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To clarify, we have made the following change: Original text: “Inorganic salts commonly found in the atmosphere (e.g. sodium chloride and ammonium sulphate) have only a small effect on the surface tension in aqueous solution . . .” Modified text: “The surface tension of an aqueous solution containing only an inorganic salt (e.g. sodium chloride or ammonium sulphate) is only slightly higher than the surface tension of pure water. . .”

”P17984 L10: Please include CCN studies of model mixtures: Broekhuizen et al, 2004 et al., Padro et al., 2007.”

Page 17984, lines 11-12: The references have been inserted in text Pages 18002 and 18004: The references have been added in the reference list

“P17990 L14. & P17992 L12 What is the concentration range relevant for activation?”

Page 17990, line 14: The following text has been inserted: “(GF = 3-12 for particles with diameters in the range 30-100 nm)” Page 17992, line 12: The following text has been inserted: “GF = 3-12”

“P17985 L22. Please refer to the density –ion coefficient; Wex et al, 2007”

Page 17987, line 9: The following has been inserted: “Water activity has been described by a number of different one-parameter approaches: for example the combined effect of density, molar mass and degree of dissociation on water activity has been described by the so-called ionic density, \tilde{A}_{ion} (Wex et al., 2007). (. . .) Rissler et al. 2010 have compared the performance of five such one-parameter approaches including κ and the ionic density, \tilde{A}_{ion} .”

“P17999 L12. What is the paper reference to this citation?”

The following reference has been inserted on page 18002: Asa-Awuku, A., Engelhart, G.J., Lee, B.H., Pandis, S. and Nenes, A.: Relating CCN activity, volatility, and droplet growth kinetics of β -caryophyllene secondary organic aerosol, *Atmos. Chem. Phys.*, 9, 795-812, 2009

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“Table 2: Please clarify that 50:50 refers to a mass fraction”

Page 18008. The following change has been made in the caption to table 2. Original text: “. . .for the 50:50 mixtures between an organic acid and ammonium sulphate (AS).” Modified text: “. . .for the mixtures with 50:50 mass ratio between an organic acid and ammonium sulphate (AS)”

“Fig1. Is there a fit for OA + AS? There are 6 measurement points plus 2 models (Pure CPA and Water) but only 7 fits presented.”

Page 17990, Line 9. The following sentence has been inserted: “No fit is shown for the mixture of oxalic acid and ammonium sulphate, because the surface tension depression of these mixtures is negligible.”

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 10, 17981, 2010.

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