

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

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Interactive comments on “Joint effect of organic acids and inorganic salts on cloud droplet activation” by M. Frosch et al. Anonymous Referee #1

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 improved/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

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particle diameter of 35 and 100 nm and also include experimental values for comparison.

"The authors present laboratory results of on the CCN ability of mixed organic/inorganic particles. The presented results fit well in the discussion of previous studies that are, however, not properly discussed in the current study."

References to several additional studies have now been included in the discussion (see details in the following comments).

"This paper is one among many others on the same topic (CCN ability of organics, mixed particles). It is clearly unfeasible to explore all possible combinations of atmospheric compositions, species and mixing ratios in particles but the current study shows once more that relatively simple assumptions lead to reasonable predictions of CCN activity. Instead of adding more complexity to the descriptions of aerosol effects on clouds, a more general description is desired and it should be clearly pointed out under what circumstances deviations from common approaches (e.g., Köhler equation) can be expected."

We conclude (on page 18001, line 8ff) that Köhler theory (based on parameterizations of surface tension and water activity) cannot be used to model measured critical supersaturation when the organic is a strong surfactant nor for the mixtures containing sodium chloride and oxalic acid. In the latter case Köhler theory probably fails due to solubility effects.

"In addition of a discussion of the broader impacts of the results to the aerosol indirect effect, there are several unclear sections in the paper that need to be addressed before it can be considered for publication."

We focus on the microphysics of water uptake and activation of aerosol particles. An analysis of the broader impacts of our results on the aerosol indirect effect is therefore out of scope of this study. However, we have included references to the following stud-

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ies on the aerosol indirect effect: Page 17983, line 12: "e.g. Twomey, 1984; Albrecht, 1989" Page 18001ff: The references has been added to the list.

"General comments"

"1) The authors show that for most systems simple assumptions based on Köhler theory lead to reasonable good predictions of supersaturation. This result should be highlighted much stronger throughout the paper (and in the abstract). Regarding the high complexity of particle compositions, it is necessary to find simplified descriptions for their representation in models. How common are the systems in the atmosphere where common assumptions fail (e.g., high fractions of NRFA, mixtures with high mass fractions of oxalic acid, ...)?"

While it may not be likely to find an atmospheric particle where oxalic acid comprises 50% of the mass, particles with a large mass fraction of organic material seem to be common (as for example reported by Jimenez et al. (Science, 326, 1525-1529, 2009)). The particles in this work serve as model systems to understand the microphysics in cloud droplet activation of particles with a large mass fraction of organic material. We do show that for many mixed systems, Köhler theory leads to reasonably good predictions of critical supersaturation. However, for some mixtures great deviations (quantified below) are observed. In the abstract (page 17982, line 24f) we note that Köhler compared well with measurements with a few exceptions, and in the conclusion (page 18001, line 8ff) we also mention the mixtures for which Köhler theory accurately predicted critical supersaturation.

"The authors use terms like 'considerable' and 'significantly' to describe deviations from Köhler equation for several systems. Can those be better quantified? In particular, the authors should mention the implications to 'real clouds' where it has been shown that in dynamic systems (as opposed to equilibrium situations as in CCN counters) composition effects are even further reduced (e.g., [Ervens et al., 2010; Feingold, 2003])"

The following text has been inserted: Page 17983, line 15: "In the atmosphere the

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formation of cloud droplets is determined by the size distribution and chemical composition of the cloud condensation nuclei as well as dynamic parameters such as updraft velocity and liquid water content (e.g. Nenes, et al., 2002; Feingold, 2003; Lance et al., 2004, Koehler et al., 2006, Ervens et al., 2010). The relative importance of these effects is not yet fully clarified. In this work we address the effect of particle chemical composition on the critical supersaturation.” Page 18003: References have been added to list. To quantify deviations from Köhler theory, we provide deviations between predicted and experimental values in percent at relevant places in the revised manuscript.

"2) The authors explain in great detail at several places in the manuscript that a low molecular weight, high density and high degree of dissociation decrease the water activity and thus make 'good CCN'. This concept is not new as it follows directly from Köhler equation. The effect of these parameters on water activity has been parameterized by the hygroscopicity parameter ('kappa') [Petters and Kreidenweis, 2007] that should be discussed here. Most of the results of the present study can be explained by the additive character of this parameter. Since kappa has been used so widely for similar systems I suggest to add a column to Figure 5 (or replace column 'Entities per volume dry aerosol' as it is directly proportional to kappa and is just an unnecessary additional parameter) with the corresponding kappa values."

An extra column with kappa values has been inserted in Table 5. Furthermore, a new table (Table 7) has been created which compares kappa values derived from our CCN measurements to kappa values calculated using the mixing rule given by Petters and Kreidenweis. Kappa values for individual compounds are obtained from literature when available and otherwise estimated according to Sullivan et al. 2008. Text has been inserted in the revised manuscript accordingly: Page 17987, line 9: "Here we apply the widely used single hygroscopicity parameter, κ , described by Petters and Kreidenweis (2007) $1/a_w = 1 + \kappa \cdot V_s/V_w$ (6) where V_s and V_w are the volumes of dry particulate matter and water, respectively. For multicomponent systems, the overall value of κ

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is given by the simple mixing rule: $k = S(e_i \cdot \kappa_i)$ (7) where ε_i is the volume fraction and κ_i is the single hygroscopicity parameter of component i . Rissler et al. 2010 have compared the performance of five such one-parameter approaches including κ and the ionic density, ρ_{ion} ." Page 17996, line 25: "Critical diameters and growth factors have been determined for two dry particle diameters and are listed in Table 7, together with measured and estimated κ values." Page 17997, line 4: "For example, a particle with diameter 60 nm is predicted to activate at a supersaturation of 0.31%, but is found to activate at 0.40%, corresponding to an underprediction of 29%. This will be discussed below. These deviations are also reflected in the differences between the measured and estimated values of κ (see Table 7) for the sodium chloride/oxalic acid particles. For the mixtures of oxalic acid and ammonium sulphate the κ values derived from CCN measurements agree well with estimated κ values. It should be noted that it is an underlying assumption that κ does not depend on solute concentration (i.e. growth factor). The reported κ_{meas} is thus calculated as the average of the κ 's obtained from the measured critical supersaturation for a range of dry particle sizes (Table 6). κ_{est} is estimated from CCN derived κ values reported by Petters and Kreidenweis (2007). Petters et al. (2009) or determined using the method of Sullivan et al. (2009)." Page 17998, line 1: "The deviations between κ_{est} and κ_{meas} (see Table 7) are within experimental uncertainty for the mixtures containing succinic acid or adipic acid. For the mixtures containing citric acid the deviations are greater. However, a CCN derived value of κ for citric acid could not be found in literature and was determined according to Sullivan et al. (2009)." Page 17998, line 13: " κ_{est} for NRFA is determined according to Sullivan et al. (2009); the deviation from κ_{meas} is 25%. κ_{meas} is not available for the mixtures containing cis-pinonic acid (see Table 7)."

"3) The results of the current study are expressed as a function of a growth factor GF. The usefulness of this parameter is not really obvious to me. Here, GF is used to represent a certain solute concentration (i.e. water/solute ratio). Usually GF for different compounds are compared at the same relative humidity and thus, give a measure for the amount of water uptake under the same conditions. How meaningful is the range

of GF shown in Figs 3-6 for the water uptake at activation? For each particle, a critical radius can be calculated that represents the particle size at the point of activation (cf. [Pruppacher and Klett, 2003]). What GF corresponds to the critical size of the particles?"

Page 17988, line 7: The following text has been inserted: "In this study, critical supersaturations have been determined for internally mixed particles with diameters between 30 and 100 nm. The growth factors at activation of these particles are in the range 3-12."

"Specific comments"

"p. 17982, l. 13: reword 'the more significant term in the Köhler equation'. I assume that you want to say that there were only differences in the Raoult term for the different mixtures but not in the Kelvin term."

The text has been removed:

"- p. 17982, l. 19: reword 'higher effect on water activity': The relative contributions of water activity vs Kelvin effect are not explored here. Is it meant here that inorganics have a smaller Raoult term (higher kappa)."

The text have been modified as suggested: Original text: "...inorganic compounds had a higher effect on water activity than the studied organic acids and increasing..." Modified text "...inorganic salts are predicted to have a smaller Raoult term than the studied organic acids. Increasing..."

"p. 17983, l. 1-3: In the abstract the error should be quantified that is introduced if no surface partitioning for these systems is assumed."

The following text has been inserted: p. 17983, l. 1-3: "with deviations above 50% for a 60 nm particle containing 50% (dry mass) of Nordic reference fulvic acid"

"p. 17983, l. 17/18: It is true that not for all species (mixtures) CCN activity has been

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explored in detail. However, it should be noted here that it might not be necessary as sufficient frameworks are available (e.g., kappa) that allow a reasonable estimate."

As mentioned above, a new table has been created (Table 7) listing the kappa values of the mixtures (based on the mixing rule of κ). Also, the following text has been inserted: Page 17987, line 7: "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, ρ_{ion} (Wex et al., 2007)."

"p. 17985, l. 24 (and other places, too): Reword 'produce more species', e.g. replace by 'dissociate into more ions'."

Page 17985, Line 24 AND Page 17992, Line 20: The text have been modified as suggested: Original text: "produce more species (molecules or ions)" Modified text: "dissociate into more ions"

"p. 17987, l. 11: 'activates and takes up water'. A growth factor greater than 1 means that the particles take up water but do not necessarily activate yet. Activation requires that the wet particle sizes exceed the critical radius as can be derived to describe the maximum of the Köhler curve."

Page 17987, Line 11 The text have been modified as suggested: Original text: "activates and takes up water" Modified text: "takes up water"

"p. 17990, l. 19 ff: How do the parameterizations of surface tension for other pure compounds (e.g., [Ervens et al., 2004; Tuckermann and Cammenga, 2005; Tuckermann, 2007] compare to those you show in Figure 1 and Table 3? Can they be applied in order to reduce complexity in CCN representations (i.e. avoiding additional equations)? How significant is surface tension suppression at the point of activation (i.e. where would critical radii fall on the scale of GF in Figure 3)? Is the fact that the surface tension suppression in organic/inorganic mixtures is less than for pure organics simply a con-

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centration effect? I.e. inorganics usually contribute more water to the particle and thus, the organics can dissolve into a larger volume which results in a lower concentration."

The droplet diameters at activation have been inserted into Table 7 (see above).

"The parametrizations of surface tension for other pure compounds themselves differ a lot from each other and depend very much on the individual compound studied. For example, the concentration of a pure organic compound necessary to decrease the surface tension of pure water from 73 mN/m to 68 mN/m is 0.25 mg/mL, 0.6 mg/mL, 0.9 mg/mL and 4 mg/mL for azelaic acid, pinonic acid, humic acid and 3-hydroxybutanoic acid, respectively while levoglucosan and 3-hydroxybenzoic acid cannot decrease the surface tension to such extent even at a concentration of 5 mg/mL (Tuckermann and Cammenga, 2004) Consequently, the complexity in CCN representations cannot be reduced by using a "universal" surface tension function. "

As written in our answer to general comment 3, the growth factors at activation of these particles are in the range 3-12 and surface tension depression at activation is also compound dependent. We think that the lower surface tension in organic/inorganic mixtures as compared to pure organics at a given GF is a concentration effect. At GF=6 the concentration of cis-pinonic acid in the droplet formed on a mixed article is 0.2526 m/m% and using the surface tension data from Tuckermann and Cammenga (2004) or the parametrization from Varga et al. (2007) this concentration leads to a surface tension value of 61-61.5±0.6 mN/m. This fits well with the value (62±0.6 mN/m) obtained for the the mixed solution corresponding to GF = 6 (Figure 1). Page 17990, line 26: We have added the following text: "At GF = 6 the concentration of cis-pinonic acid in the droplet formed on a mixed particle is 0.252 w/w% and using the surface tension data from Tuckermann and Cammenga (2004) or the parametrization from Varga et al. (2007) this concentration leads to a surface tension value of 61-61.5±0.6 mN/m. This fits well with the value (62±0.6 mN/m) obtained for the mixed solution corresponding to GF = 6 (see Fig. 1)."

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"p. 17991, l. 25 ff: is the surface tension reduction by NRFA comparable to other similar molecules (e.g., humic acid, or levoglucosan) [Tuckermann and Cammenga, 2005; Tuckermann, 2007]?"

The surface tension reduction by NRFA is slightly stronger than that caused by the humic acid sodium salt studied by Tuckermann and Cammenga (2005) or Tuckermann (2007). This is not surprising, since the composition of fulvic acids differ from that of humic acid. Furthermore, different humic acids influence the surface tension to different extents depending on the aromatic/aliphatic character of the humic substance. The surface tension effects of such compounds (NRFA, SRFA, aromatic and aliphatic humic acids, HULIS with and without ammonium sulfate) have been compared by Kiss et al. (2005). The surface tension reduction by NRFA is substantially different from that of levoglucosan since levoglucosan is an anhydro sugar the properties of which are fundamentally different from the properties of NRFA. Levoglucosan did not show surface tension reduction in the concentration range studied by Tuckermann and Cammenga (2005). We have omitted lines 25-28 on page 17991.

"p. 17992, l. 11/12: 'water activity will be the main factor determining supersaturation'. Do you mean that the surface tension suppression is minor as compared to the effect on water activity and thus different compositions affect water activity but not surface tension?"

Correct. We conclude in section 4.1 that surface tension suppression is negligible for the mentioned mixtures within the studied concentration range. In the following section we find that the chemical composition and concentration has a much greater effect on water activity. The text have been modified as follows: Original text: "... water activity will be the main factor determining critical supersaturation..." Modified text: "... water activity will be more significant when determining critical supersaturation ..."

"p. 17993, l. 26 ff: this discussion is trivial and can be removed or shortened as it directly follows from Equation 1."

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Page 17993, line 26ff: Original text: "The higher density and lower molecular weight of sodium chloride result in a higher concentration of dissociated sodium chloride entities at a concentration corresponding to $GF = 4$ (see Table 5) and a lower water activity at a given growth factor in aqueous solutions of pure sodium chloride than in mixtures of oxalic acid and ammonium sulphate. Consequently, a higher mass fraction of sodium chloride in aerosol particles containing oxalic acid – or a compound with similar physical and chemical properties – corresponds to lower water activity and thereby also a greater ability to act as CCN at a given supersaturation. Furthermore, sodium chloride has a greater effect on water activity than ammonium sulphate. This can be seen from Fig. 4b, where water activity of the mixtures containing sodium chloride is lower than the water activity of the two mixtures containing ammonium sulphate for all growth factors. This is most clearly seen by a comparison with the curve showing the modeled water activity of pure oxalic acid (dotted black line) which is shown in both Fig. 4a and Fig. 4b." Modified text: "The higher density and lower molecular weight of sodium chloride result in a higher concentration of dissociated sodium chloride entities at a concentration corresponding to $GF = 4$ (see Table 5) and a lower water activity at a given growth factor in aqueous solutions of pure sodium chloride than in mixtures of oxalic acid and ammonium sulphate.

"p. 18001, l. 2/3: AIM has been applied to many atmospheric applications. So, the statement that it was found that it indeed works sounds somewhat presumptuous."

Page 18001, line 2-3: The sentence has been omitted from the manuscript Also, the following sentence has been removed from the conclusion: Page 18001, line 4-5: "confirming the atmospheric relevance of this thermodynamic model"

"p. 18001, l. 14 ff: Could the 'unusual behavior' of the NaCl/oxalate mixture be a result of salt formation? The hygroscopic properties of Na-oxalate might be different than for NaCl. Though I understand that the performed experiments were not designed to explore such effects, it might be worth to raise this possibility."

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The solubility of oxalic acid is almost the same as the solubility of sodium oxalate (approximately 4 g/100 g water). The formation of sodium oxalate is therefore not a likely explanation of the “unusual behaviour” reported in this study. Nevertheless, salt formation is of course important to keep in mind, and we have inserted the following text: Page 17999, line 2: “For mixtures there may also the possibility of a slightly soluble salt forming.”

"Technical comments"

"p. 17982, l. 12: negligible"

The spelling error has been corrected

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