

Interactive comment on “Tight coupling of particle size and composition in atmospheric cloud droplet activation” by D. Topping and G. McFiggans

Anonymous Referee #2

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Topping and McFiggans present model calculations and discussion on the coupling of particle size and particle composition with regards to activation of aerosol particles to cloud droplets. Based on an extended Köhler theory, including the effects of co-condensation of semivolatile organic gases on hygroscopic aerosols, it is shown that co-condensation might be an important influence on the critical saturation ratio for droplet activation and related particle dry size. The authors also discuss implications and potential issues with respect to characteristic time-scales and supersaturation conditions in instruments used for cloud droplet activation experiments, as compared to the conditions in the ambient atmosphere. The equilibrium partitioning type of model calculations lead to interesting results and this paper is of relevance for atmospheric chemistry and physics.

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I recommend this article for publication in ACP, after the comments listed below have been adequately addressed.

General comments

The manuscript is written in a concise way for the most part, however, there is little information given about how exactly the calculations were carried out and what assumptions are made (e.g., monodisperse aerosol population, instantaneous equilibrium vs. dynamic condensation of organics, gas phase representation, i.e., depletion of gas-phase organic vapors during co-condensation, dilution of air masses and reduction of organic saturation ratio at cloud condensation level...). I would like to see more information on the modeling approach and implied assumptions. Furthermore, some of the statements in the text need additional clarification to avoid ambiguous interpretation by the reader, as pointed out in the specific comments below.

The calculations in the manuscript are restricted to purely organic aerosols and co-condensation of water and organics to such mixtures. In the troposphere, many aerosols will be mixtures of soluble inorganics and hydrophobic as well as hydrophilic/hygroscopic organics. Can the authors comment on how such mixtures could influence their findings?

Do the authors mainly think of aerosol-to-cloud droplet activation in the lower troposphere (boundary layer), where organic vapors are likely more abundant than in the higher regions of the troposphere or in the updrafts of a deep convective cloud? Related to that, do the authors think that co-condensation of organic vapors to non-activated particles can keep up with typical vertical velocities and associated water condensation in convective cloud formation or could it be that in such cases kinetic limitations will become important, limiting the co-condensation effect?

Specific comments and corrections

Abstract

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line 1: The first sentence is rather ambiguously formulated and rewording is suggested. "The substantial uncertainty in the indirect effect on radiative forcing in large part arises from the influences of atmospheric aerosol particles on (i) the brightness of clouds, exerting significant shortwave cooling with no appreciable compensation in the longwave, and on (ii) their ability to precipitate, with implications for cloud cover and lifetime." – "indirect effect" of what (aerosols)? "and on (ii) their ability" to what should "their" refer to?

line 7: "derived in 1936", better: derived by Köhler (1936). Otherwise it is not even clear that 1936 denotes a year.

line 13: "as the ambient humidity increases has larger implications", maybe: "has potentially larger implications", since the dynamic mass transfer and potential limitations thereof are not considered in the calculations.

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Eq. (1): RT in the denominator should be in italic case. It is a common mistake to write $\frac{RH}{100}$ when RH is in "units" of %, since % already means per 100, the denominator should actually be 100 % (= 1), so just write RH. It might also be useful here to show the relationship to the partial pressure and pure compound vapor pressure, as in Eq. (A1).

line 5: "where RH in the", spelling: is. It could further be noted that here it is RH with respect to liquid water. a_w is the mole fraction-based water activity in a solution.

line 6: check unit of molar volume.

line 11: "above a droplet as a result of its size", better: above a spherical droplet as a result of its curvature (size).

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line 9: "Ambient vapour pressures of atmospherically important compounds are likely to be < 0.1 Pa and,". I guess, you mean here atmospherically important organic

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compounds related to gas-particle partitioning? Otherwise this statement is incorrect, there are many important trace gases with higher vapor pressures. line 13: “Until the current work, it has not been possible to solve the equilibrium for semi-volatile systems with more than two co-condensing gases”; “it has not been possible” is a rather bold statement as actually the equations for gas-particle partitioning with many compounds have been developed and used before in many studies. Only the size-dependence has not been considered.

line 23: “dry size particles”. At this point it might be good to clearly define what is meant by “dry size particles” or “dry conditions” as compared to “effective dry particle size” mentioned on the following page. This is important terminology in this study, as “dry” is not equal to “without water”, but is also related to the loss/condensation of other semivolatile species (?).

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line 4: “resulting from removal of surface active molecules to the surface of the particle from the bulk”. This sentence is rather confusing, I suggest rewording.

line 26: “It should be emphasized here that the effects of non-ideality are explicitly considered and hence the “water affinity” of the condensing organic compounds is directly incorporated into the predictions.” This is an important point that should be further discussed. As particles are expected to be dilute aqueous solutions close to activation, the water affinity or hydrophilicity of organic compounds is likely an important property for efficient co-condensation. Hydrophobic organics (HOA) will probably not significantly co-condensate to the aerosols. Therefore, the types of organic compounds that have an effect on the critical supersaturation are mostly hydrophilic “OOA-like” organics, which are mostly partitioned to the aerosol phase already at sub-saturated RH according to Cappa and Jimenez (2010). What are typical O:C ratios of the 2727 compounds used in the calculations, are these representative for ambient air?

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first paragraph: How was the non-ideality in case of the volatility distributions of Cappa and Jimenez (2010) considered? BVOC compounds are later discussed as efficient co-condensates with respect to critical supersaturation. However, the higher SVOC and IVOC volatility range of BVOC compounds, that could potentially co-condensate to growing particles (as these species are to a substantial fraction in the gas phase at dry conditions), are also the less-oxidized fractions of the BVOC class (e.g., Donahue et al., Atmos. Chem. Phys. Discuss., 11, 24883-24931, 2011) and therefore might not condense substantially on a highly dilute aqueous aerosol (e.g., Zuend et al., Atmos. Chem. Phys., 10, 7795–7820, 2010). Can the authors comment on these points and whether such behavior is found/considered in their calculations?

Appendix A, page 25163

Eq. (A1): While this equation is correct, many organic compounds will not be supersaturated or close to saturation in the atmosphere; they will also not show runaway-growth behavior. Is it therefore mostly the activity factor, and the effect of organic condensation on the water activity (dilution by organic condensation) that is important regarding the co-condensation of organics?

line 18: for clarity write “mole fraction-based activity coefficient f_i ”.

lines 19 - 22: “For the Master Chemical Mechanism (Jenkin et al., 1997) simulations, the model UNIFAC (Fredenslund et al., 1975) was used to calculate non-ideality and that the calculations including the volatility representations of Cappa and Jimenez (2010) are ideal.” The second part after “non-ideality and” is unclear, missing some clarifying words. By “the volatility representations of Cappa and Jimenez (2010) are ideal”, do the authors mean that the C^* of the volatility distributions assume ideal mixing, or is here meant that the calculations with those volatility distributions were carried out assuming ideal mixing in the aerosol phase?! If the latter is the case, this should be mentioned in Section 1 of the main text. It would likely also have important consequences as mentioned in the points above, potentially significantly altering the

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results of the model calculations when non-ideality is considered.

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line 14: “a decrease in temperature of 15K leads to a predicted increase in condensed organic mass of around 1.6.” Unclear what “of around 1.6” means (what unit?); should it read “by a factor of 1.6”?

Fig. 1

It would be good to mention the change in scaling of the y-axis above a value of 1.

Fig. 2

Change the y-axis label and caption. I guess what is actually shown is “ $S_{\text{crit}} - 100\%$ ”?

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 25155, 2011.

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