

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

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.

Response: We apologise for the lack of clarity. Following the response to referee#1, the condensed mass in figure 1, an aerosol comprised of 30% core material at 0%RH, would correspond to a number concentration of ~600/cc. If we were able to solve the equilibrium across different sizes for higher concentrations, the amount of condensed material per particle would decrease. Conversely at lower concentrations the amount would increase. The cerise area displayed in figure 1 would then either move toward the grey areas representing Köhler theory resulting in higher critical supersaturations or diverge away, respectively. We have added two arrows to figure 1 to highlight this. The reviewer has also raised a very important point in that this precursor study suggests size, composition and **number** remain coupled. We suggest the title of the paper now becomes: **'Tight coupling of particle size, number and composition in atmospheric cloud droplet activation'**. We are not solving equilibrium between different sized particles; rather we are following the methodical approach of Kulmala et al (1993) in first studying single particle effects and highlighting the true applicability of traditional Köhler theory. Dynamical simulations across multiple sizes are the basis of ongoing investigations and will form the focus of a future publication in which we assess the atmospherically realistic effect of co-condensation on cloud droplet number concentrations. Following the addition of arrows to Figure 1, we have also added similar arrows to figure 2. We also now suggest adding the following text to the discussion of figure 1 on line 26 page 25159: *'The actual amount of soluble material condensing per particle will depend on the size distribution and number concentration. In this example, the multicolored arrows indicate the direction the coloured areas would follow on increasing and decreasing the concentration of particles. The shape of the size distribution, concentration, volatility profile and amount of condensable material will dictate this final result, a solution of the condensation dynamics the focus of future work.'* Following the discussion of figure 2, a similar line will be placed at line 14 page 25160: *'The block arrows indicate the effect changing the particulate concentration would have on the amount of additional condensed soluble material per particle through co-condensation, thus critical saturation ratio.'*

One novel aspect of this paper is the ability to account for an unlimited number of semi-volatiles in the equilibrium calculation of critical saturation ratios, which hasn't been presented before this work. In addition, the paper provides important considerations when measuring single particle hygroscopicity of organic aerosol, and the potential role of co-condensation in currently reported discrepancies, as we discuss in the manuscript. Following

the above discussion and response to reviewer #1 we suggest the following text is added at the end of section 1: *'In these simulations we have not solved equilibrium between different sized particles or accounted for the concentration of particles as a function of size. Nonetheless, following the previous studies of Kulmala et al (1993), the results in figure 1 highlight the inherent limitations of using traditional Kohler theory in the presence of semi-volatile organic compounds, including the difficulties in determining single particle hygroscopicity through laboratory studies as discussed in the following section. This would suggest that size, number and composition remain inherently coupled whenever there semi-volatile material is present at reasonable atmospheric concentrations. To assess the true potential effect on cloud activation, thus cloud droplet number concentrations, the condensation dynamics has to be solved with appropriate aerosol size distributions. This is the basis of ongoing investigation.'* We also suggest the following modification to the abstract, line 15, page 25156: *'owing to inextricable linkage between the aerosol composition, particles size and concentration under ambient conditions.'*

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?

Response: We are currently able to incorporate the effect of inorganic-organic interactions on the equilibrium vapour pressure above a one liquid phase droplet using benchmark activity coefficient models such as AIOMFAC (Zuend et al 2011). Furthermore, the simulations presented in the paper consider organics, insoluble cores and inorganic cores. The focus of the paper is to highlight the inaccuracy in assuming semi-volatile compound will not re-equilibrate between the gas and condensed phase, at changing ambient conditions, when assessing the relationship between size, composition and hygroscopicity. Even without addressing all the aspects the reviewer outlines, this still holds. With regard to the potential influence of inorganics it would be dangerous to speculate too much without results from future simulations. The relative amount of inorganic compounds relative to hydrophilic/hydrophobic organics would dictate the net effect of salting in/salting out on the overall condensed mass of a one liquid phase droplet. This in turn would change the potential effect of co-condensation displayed in figure 1 and 2. Zuend et al (2010) used a six-component system and the AIOMFAC model to suggest that liquid-liquid equilibrium is prevalent in mixed inorganic/organic aerosol, the overall effect being a reduction in condensed SOA mass as compared to a single-phase system. On the other hand, Barley et al (2011) used 2727 compounds from the MCM model and demonstrated that the likelihood of phase separation depends on the gas phase composition and ambient conditions. Whilst there are additional considerations to using the volatility representations of Cappa and Jimenez (2010) in our simulations, for example, the results from this study highlight that current representations of aerosol hygroscopicity may not be truly representative of behaviour in the atmosphere.

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?

Response: The solution of the condensation dynamics, and sensitivities to parameters used within that, is the focus of ongoing work and speculation on the future results must remain out of the scope of the present study.

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?

Response: We suggest adding the text 'of aerosol particles' after the first instance of the 'indirect effect'.

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

Response: This has been changed.

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.

Response: We agree and this has been changed.

page 25157 Eq. (1): RT in the denominator should be in italic case. It is a common mistake to write RH when RH is in "units" of %, since % already means per 100, the denominator 100 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).

Response: This has been changed and an additional relationship relating partial pressure to pure component vapour pressure inserted.

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.

Response: This has been changed

line 6: check unit of molar volume.

Response: Apologies, this has been corrected to $(\text{m}^3 \text{mol}^{-1})$.

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

Response: This has been changed.

page 25158 line 9: "Ambient vapour pressures of atmospherically important compounds are likely to be $< 0.1 \text{ Pa}$ and,". I guess, you mean here atmospherically important organic compounds related to gas-particle partitioning? Otherwise this statement is incorrect, there are many important trace gases with higher vapor pressures.

Response. This is correct. We have made the following addition to the text: "With respect to gas-particle partitioning, ambient vapour pressures of atmospherically important compounds are likely to be $< 0.1 \text{ Pa}$ and..'

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.*

Response: Here we are referring to the lack of prior evidence of simultaneous solution of equilibrium partitioning for more than two co-condensing gases on cloud activation potential. We suggest the following addition: ‘Until the current work, the effect of co-condensing vapours on cloud activation potential has not been reported for more than two co-condensing gases.’

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 (?).*

Response: In this study, ‘dry size’ does refer to the size of a particle at 0%RH, thus without water. The ‘effective dry particle size’ is that which would result in the same critical saturation ratio after accounting for co-condensation.

page 25159 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.*

Response: This has been reworded “resulting from movement of surface active molecules from the bulk to the surface of the particle”

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).*

Response: The results presented in figure 2 show that for the ideal simulations, when there is significant amount of material left in higher volatility bins ($>C^*=0$) after partitioning at sub-saturated RH, there is a marked decrease in critical saturation ratio through the addition of more solute at higher RH. The correlation of activity coefficients versus volatility may have an important role in dictating the overall impact of co-condensation of separate volatility profiles, as discussed above. Unfortunately current 2D representations of activity coefficient versus volatility (Donahue et al 2011)) are not able to capture the potential for both salting in and salting out (Barley et al 2010, Topping et al 2011). Further work is therefore required using output from detailed gas phase mechanisms.

What are typical O:C ratios of the 2727 compounds used in the calculations, are these representative for ambient air?

Response: As discussed in Barley et al (2011), the most abundant condensed molecules have a molar mass in the range 150- 220 and an O:C ratio of 0.5 to 1.0, the average value for the aerosol dependent on the choice of vapour pressure method used in partitioning calculations. Generally, this average O:C ratio is higher than the O:C ratio reported in recent studies of atmospheric aerosol in heavily urbanised areas: generally below 0.5 in London (Allan et al.,

2010), and 0.36 in the New York area (Sun et al., 2011); but similar to the value of up to 0.8 for aged aerosol measured in the outflow from Mexico city (DeCarlo et al., 2008).

page 25160

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?

Response. We have not included the effects of non-ideality for the volatility distributions of Cappa and Jimenez (2010). Please refer to the previous response.

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?

Response: The effect of organic condensation on the increase in solute mass, thus effect on water activity, is the process dictating the decreased critical saturation ratio presented here. The simultaneous solution of the equations for all components is not reliant on their runaway growth. The main effect of co-condensation isn't the runaway growth in organic vapours, but the increasing "water-soluble particle mass" with increasing RH.

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

Response: This has been corrected

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

Response: The partitioning calculations using the volatility representations of Cappa and Jimenez (2010) were carried out assuming unity activity coefficients. The response to potential implications is made earlier on in this document.

page 25164

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"?

Response: Yes it should, this has been corrected.

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

Response: The following text has been added to the caption: 'Above a saturation ratio of 1 the axis scale has been changed to more clearly display the critical point.'

Fig. 2 Change the y-axis label and caption. I guess what is actually shown is "Scrit - 100 %"?

Response: This is correct, the label has been changed accordingly.

References:

Allan, J. D., Williams, P. I., Morgan, W. T., Martin, C. L., Flynn, M. J., Lee, J., Nemitz, E., Phillips, G. J., Gallagher, M. W., and Coe, H.: Contributions from transport, solid fuel burning and cooking to primary organic aerosols in two UK cities, *Atmos. Chem. Phys.*, 10, 647–668, doi:10.5194/acp-10-647-2010, 2010.

Barley, M. H., Topping, D., Lowe, D., Utembe, S., and McFiggans, G.: The sensitivity of secondary organic aerosol (SOA) component partitioning to the predictions of component properties – Part 3: Investigation of condensed compounds generated by a near-explicit model of VOC oxidation, *Atmos. Chem. Phys.*, 11, 13145–13159, doi:10.5194/acp-11-13145-2011, 2011.

DeCarlo, P. F., Dunlea, E. J., Kimmel, J. R., Aiken, A. C., Sueper, D., Crouse, J., Wennberg, P. O., Emmons, L., Shinozuka, Y., Clarke, A., Zhou, J., Tomlinson, J., Collins, D. R., Knapp, D., Weinheimer, A. J., Montzka, D. D., Campos, T., and Jimenez, J. L.: Fast airborne aerosol size and chemistry measurements above Mexico City and Central Mexico during the MILAGRO campaign, *Atmos. Chem. Phys.*, 8, 4027–4048, doi:10.5194/acp-8-4027-2008, 2008.

Donahue, N. M., Epstein, S. A., Pandis, S. N., and Robinson, A. L.: A two-dimensional volatility basis set: 1. organic-aerosol mixing thermodynamics, *Atmos. Chem. Phys.*, 11, 3303–3318, doi:10.5194/acp-11-3303-2011, 2011.

Sun, Y.-L., Zhang, Q., Schwab, J. J., Demerjian, K. L., Chen, W.-N., Bae, M.-S., Hung, H.-M., Hogrefe, O., Frank, B., Rattigan, O. V., and Lin, Y.-C.: Characterization of the sources and processes of organic and inorganic aerosols in New York city with a high-resolution time-of-flight aerosol mass spectrometer, *Atmos. Chem. Phys.*, 11, 1581–1602, doi:10.5194/acp-11-1581-2011, 2011.

Zuend, A., Marcolli, C., Peter, T., and Seinfeld, J. H.: Computation of liquid-liquid equilibria and phase stabilities: implications for RH-dependent gas/particle partitioning of organic-inorganic aerosols, *Atmos. Chem. Phys.*, 10, 7795–7820, doi:10.5194/acp-10-7795-2010, 2010.

Zuend, A., Marcolli, C., Booth, A. M., Lienhard, D. M., Soonsin, V., Krieger, U. K., Topping, D. O., McFiggans, G., Peter, T., and Seinfeld, J. H.: New and extended parameterization of the thermodynamic model AIOMFAC: calculation of activity coefficients for organic-inorganic mixtures containing carboxyl, hydroxyl, carbonyl, ether, ester, alkenyl, alkyl, and aromatic functional groups, *Atmos. Chem. Phys.*, 11, 9155–9206, doi:10.5194/acp-11-9155-2011b