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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Connecting the solubility and CCN activation of complex organic aerosols: a theoretical study using the Solubility Basis Set (SBS)" *by* I. Riipinen et al.

Anonymous Referee #1

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The paper is clearly in scope of ACP and presents some important results and discussions of the behaviour of particles comprising mixtures of components of varying solubility. In particular, there is little work exploring the sensitivity of CCN behaviour to varying shapes of organic solubility distribution and this work addresses this gap. The study provides an excellent evaluation of three commonly employed assumptions in CCN activation, within the bounds of the presented analyses. I have a number of observations and concerns that the authors should consider prior to acceptance in ACP.

i) I am very unsure of, and uncomfortable with, the use of the terminology Basis Set in

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the context of the current study. It makes no sense in terms of the common usage in theoretical and computational chemistry, nor that in linear algebra. Its usage in terms of the well-established VBS was also difficult to understand and its adoption in the current work by analogy to the VBS requires explanation. As stated, the current manuscript considers "a continuous distribution of solubilities" in classes one decade apart. This provides a suitable reference scale on an appropriate axis, but I do not see where there is any reference "set" (of functions, of compounds, of properties, of vectors etc...) that can be used to make sense of the impacts of particle component solubility. This is particularly important in the context of the non-independence of the presented component description in terms of solubility and the extended volatility description where the second dimensions considers the degree of oxygenation (in terms of O:C or oxidation state), see below.

ii) To expand on this point, given the relationship between aqueous solubility of organic molecules and their polarity (and hence practically, their oxygen-containing functionality), the solubility consideration in the current paper is clearly not independent of the 2-D VBS of Donahue et al., 2011 or the Carbon number - oxidation state representation of Kroll et al., 2011. Whilst both approaches are mentioned in the current work, the relationship between the approaches is insufficiently discussed. It appears that the current work concerns itself with the cloud droplet activation behaviour of OA components, whereas the "VBS" approaches are more concerned with formation and transformation of the OA. However, the relationship between degree of oxygenation and hygroscopicity has been widely investigated, both in terms of the VBS and otherwise (e.g. in terms of AMS m/z 44 in the paper introducing the 2D-VBS). Introduction of yet another approach without contextualisation appears to add to the confusion, rather than to its clarification.

iii) Line 7 p28530 it is stated that "This assumption is justified to a first order by the different equilibration time scales of the droplets with respect to water vapour and the organic vapours in typical atmospheric conditions" when referring to the lack of consideration of partitioning of organics between the gaseous and either aqueous or non-aqueous phases in the current study. This is a bold statement. The activation is driven by the increase in water saturation ratio by cooling (updraught in a cloud, radiative or advective in a fog). The (low) rate of change of saturation ratio caused by this will lead to the mass flux of water. Since the number of water molecules is high, it is frequently assumed that the number of collisions leads much more rapid condensation of water vapour than of other components. However, the rate of change of saturation ratio of organic molecules can be very much higher (owing to both temperature, but equally or more importantly photochemical reaction). Since the vapour pressure of the organic can be very many orders of magnitude lower than water, a strong diffusion gradient between the gas phase and the particle surface can be very rapidly established. There are very many potential oxygenated organic compounds that can all be rapidly produced in response to strong emission and photochemical changes. It is far from clear to me that the addition of soluble mass to a particle in moving towards cloud base can be ignored to a first order approximation (and hence that the solubility distribution of components at lower RH will be the same as the solubility distribution of components close to activation). The Topping et al. Nature Geoscience paper (doi:10.1038/ngeo1809) should be referenced in this regard.

Again, the blurred relationship between volatility treated in the "VBS" approaches and solubility treated here is related to this. It appears conceptually peculiar to silo treatments of partitioning and water uptake into the separate approaches; the moist atmosphere is a single entity in which both processes simultaneously occur.

iv) I’m a little confused in how the approach described here to calculate the equilibration of components between the insoluble core and the surrounding aqueous shell relates to previous approaches to deal with phase separation in complex mixtures in atmospheric aerosol (notably that presented by Topping et al., 2013, doi:10.1039/C3FD00047H, which should be referenced). The solubility in the non-aqueous and aqueous phases must implicitly account for non-ideality (and e.g. degree of dissociation of weak acids

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and bases) and hence must be considered an effective solubility in the mixture. In the aqueous phase, this effective solubility may or may not be relatively simply related to the infinite dilution solubility of the component. In any case, it will very likely be relative humidity dependent. As such, the effective solubility distribution in the two phases will be RH dependent and this will (potentially significantly) affect the shape of the Kohler curves and the results illustrated in Figure 3. Coupled to the equilibration between the gas phase and the two condensed phases, it might be expected that this effect is substantial. In figure 8 a simple sensitivity to an assumed activity relationship is explored (using equation 5). Such calculations can be carried out for simple real mixtures where the activity coefficient data (albeit on a mole fraction scale) are available (and complex mixtures where the activity coefficients can be predicted). This sensitivity is assumed to constrain the real behaviour (very likely correct). It would be useful to know whether the real behaviour more normally follows one or the other of these limiting cases. Even in the absence of confirmatory experimental data, such calculations are possible.

v) It is stated on line 15 of 28532 that "... all the equations presented below can be re-derived in a relatively straightforward manner taking into account a potential difference between the mole and the mass fractions in the organic phase". This is correct, but the reference scale difference for the activity coefficients (mass or mole fraction) must be emphasised. This must be made explicit - it is the same problem as encountered in the VBS and is more important here, since the molecular weight distribution and degree of functionalisation will significantly affect effective solubility and hence phase partitioning.

Minor:

Some reference to the expected individual component effective solubility range for atmospheric components would be helpful. The very heavy functionalisation (of multifunctional peroxides, peroxyacids etc...) expected and required to attain observed O:C ratios with a measured molecular weight distribution of organics provides some surprisingly high solubilities. Along with the very low solubilities of slightly functionalised high molecular weight primary compounds, this will lead to a very wide distribution of solubilities as shown in Figure 2. Are there any data available to say whether the real atmosphere is likely to be closer to one or another of the chosen distributions? If not, what are the difficulties and are there suggested routes forward?

I am not sure that the 2 sentences in the abstract from line 17 to 21 and 21 to 24 are not contradictory. Please check. Can the stated material in the first sentence be assumed completely soluble and is this material not just a subset of the material considered within the distribution mentioned in the second sentence and hence requiring understanding of the details of its distribution in solubility? In any case, the arguments considered together in such close proximity before the reader has accessed the rest of the paper are too complicated for easy interpretation.

On p28526, 3 prior assumptions are described that are considered in the paper. The kappa consideration is not the only single parameter representation of hygroscopicity (e.g. Wex et al., 2007, doi:10.1029/2006GL028260), nor the first (e.g. Rissler et al., ACP, 2004). These treatments should be acknowledged.

It isn't clear how the presence of inorganics effects results in this paper. It is likely that there will be an inorganic fraction under most expected atmospheric conditions and this should be mentioned in the discussion.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 28523, 2014.