

## ***Interactive comment on “Influence of non-ideality on aerosol growth” by S. Compernelle et al.***

**S. Compernelle et al.**

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We thank the referee for his constructive comments and recommendations. Below we answer to all his points.

1. *I think the title is slightly confusing. The term "aerosol growth" implies a change in diameter. You do not analyse how particle dimensions alter but focus on mass transfer between the gas and particulate phase. The paper would benefit from modification of the title to reflect this.*

We agree with the referee that the term could be misleading. We replaced it by "condensation to aerosol".

2. *The authors essentially highlight that existing activity coefficient models show a lot of variability when used to model the same "atmospherically relevant" systems. This variability is slightly concerning and clearly justifies the need for further ex-*

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*perimental measurements and theoretical investigations of non-ideality on a wide variety of systems. It has been found previously that parameters which have been optimised using a subset of compounds within a given class do not necessarily work when used to model systems which include combinations of functionality not included in the original studies (e.g. Topping et al 2005; Clegg et al 2001; Tong et al 2008; Topping 2008). This in general requires a wide range of new experimental data. In some respects this brings into question the validity and strength of the statements the authors make regarding the importance of non-ideality. I can fully appreciate that this study highlights the variability of the only models which are readily available to the community. This is both important and very interesting. However I think a comment should be made regarding empirical validation of these models. Firstly, whilst the authors make adequate reference to the fact that attempts have been made to optimise versions of UNIFAC for small subsets of functionality, there are many systems encountered in secondary aerosol formation which ultimately require experimental validation. Not only that, but the theoretical basis on which various flavours of UNIFAC (those with or without inorganic ions) are based will determine how accurate these models are. However this is not entirely apparent to the reader.*

We agree with the referee that more experimental data, over more functional groups at once, is needed to determine, and improve on, the uncertainty of the used UNIFAC models. Use of parameters optimised only for subsets of compounds is indeed not ideal. Regarding the theoretical basis, even if no inorganic ions are dissolved (as we assume), UNIFAC has important, well-known limitations: no dependence of the functional group on position in the molecule and no proximity effects between two functional groups. We mention now these limitations in the text.

- 3. The authors try to bypass issues of "missing parameters" within UNIFAC through implementation of the model SPARC as an input. I would suggest caution is made*

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regarding the validity of this approach. Firstly, multiple studies have suggested that inferred interaction terms do not necessarily produce accurate results. In some instances a neglective approach has proved more accurate with respect to modelling water uptake (e.g. Topping et al 2005; Clegg et al 2001; Tong et al 2008; Topping 2008). In this study, interaction terms have been based on an untested complex theoretical model. Again, whilst the authors present this as a truly restricted avenue for improvement, ultimately these models need to be tested against reality and this should be made clear to the reader. Similarly, the validity of the SPARC method is based on its use for predicting vapour pressures.

The referee is right to be cautious on the use of another model to obtain missing parameters of the UNIFAC model. More emphasis is now put on the uncertainty in using SPARC for the missing input (see above).

Two other approaches to deal with the missing UNIFAC parameters are presented; A neglective approach, where all unknown interaction parameters are set to zero, and an analogy approach, where all unknown interaction parameters are set equal to the value of the functional group 'closest' to the unknown functional group. The analogy approach has been used before in the case of CNO2 instead of CONO2 (Chang and Pankow 2008).

We also include one extra method to calculate activity coefficients, based on a group contribution version of Hansen solubility parameters (HSP) (see e.g. "Hansen solubility parameters: a User's Handbook"). This method has been used previously with respect to organic aerosol (Jang et al. 1997). An advantage of this method is that parameters for nitrates, hydroperoxides, peroxy acids and PANs can be derived from experimental (or reliable quantum chemical data) like dipole moments and enthalpy of vaporization. From these, group contributions for  $-\text{ONO}_2$ ,  $-\text{OOH}$ ,  $-\text{C}(=\text{O})\text{OOH}$  and  $-\text{C}(=\text{O})\text{OONO}_2$  can be obtained.

4. *On page 5 lines 127-135. you make comments and references regarding the applicability of SPARC to calculate vapour pressures and thus infer activity coeffi-*

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*cients. On line 130 the authors make the comment that "SPARC produces vapour pressures that compare fairly well with experimental values". What does "fairly well" mean? Given this is a crucial parameter for predicting gasparticle partitioning I would think that more concrete statistics are required. Whilst the authors present overall statistics in table 2, this statement makes the whole paragraph confusing. I would suggest removing "fairly well". This is important because the authors then go on to state that the activity coefficient model is based on similar principles. Only at this point is the reader presented with a limitation to SPARC, which is the lack of data for peroxy acids and peroxy acyl nitrate.*

To be clearer, we rewrote the first two paragraphs of this section.

*Also, in the following paragraph the authors state that SPARC is mainly tested for infinite dilution data. Does this mean we cannot trust conclusions or model predictions made for moderately concentrated aerosols? In other words, doesn't this mean that any predictions made below an RH of say 95% is untested? This also has implications for the strength of the conclusions made.*

The SPARC-model has indeed been tested mainly for infinite dilution data, as can be found in their EPA report (Hilal et al. 2003), although some data on binary mixtures have been included, but mainly in the form of solubility data. Finally, only a comparison with experimental activities for a methanol-water mixture is included, and the statement that "The activity coefficients (or solubility) of molecules in binary solvent mixtures have been tested and appear to work well". This is the reason we chose to fit the UNIFAC parameters only to infinite dilution data of SPARC. In principle, infinite dilution data of A in B and B in A give enough constraint to get the UNIFAC interaction parameters, but we agree fully that inclusion of binary mixture data, if reliable, would have been preferable.

Finally, we have extended the discussion in section 2.4 on the comparison of the different UNIFAC versions.

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