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Interactive comment on "A curved multi-component aerosol hygroscopicity model framework: 2 – Including organics" *by* D. O. Topping et al.

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Thank you again for your general comments and support of the work which has been presented in the paper. The remarks made are addressed below.

Specific remarks. 'As in the companion paper I suggest that the authors comment on the computational effort that the model requires. In particular: How much more computer time is needed to include the organic species versus just treating inorganics? Response - As mentioned in the response to comments on the companion paper for inorganic species, we are currently implementing ADDEM within a box model to assess its suitability; our intention is to compare it with thermodynamic routines used in

3-D models within the box modelling framework to establish regimes of particular importance with regard to differences in thermodynamic descriptions. A robust profile of computational burden and comparisons with other existing models will form the focus of future work. Since no solids are allowed to form for mixed inorganic/organic systems then the iterative scheme is faster than treating just pure inorganics when solids are precipitating out of solution. A quantification of the efficiency of this has not yet been derived, but we are in the process of doing so.

'..does the iterative scheme as indicated in Fig 1 always converge quickly or are there regimes with problems to expect?' Response - Again this relates to the above response. The speed of a bisection approach in finding the root of a solution depends on the initial step length, and whether this step length can bracket the solution at the first attempt. Once the root has been bracketed then convergence is guaranteed. In this case if one is treating solid precipitation then the iterative scheme will take longer than a purely aqueous aerosols since 1) the optimisation algorithm needs more iterations for solid formation and 2) -the bracketed solution space has to be searched to see if the kohler equation can actually be satisfied (i.e. if the one boundary predicts a completely solid aerosol then the step length has to be reduced until an aqueous component is found). However, the organic model does not include solids since for mixed inorganic/organic systems, which have been studied in this paper, one can not justify treating solid precipitation using uncoupled thermodynamics. Thus for the mixed model framework one is treating a purely aqueous aerosol which is expected to converge quicker than a multiphase particle. Again the efficiency of this has not yet been quantified, but we are in the process of doing so. It is likely that an optimised step length can be found for a variety of different systems.

'..What temperature and relative humidity ranges can be considered?' Response - As mentioned in the response to the companion paper, this model was designed primarily for tropospheric conditions. This will be addressed in the revised manuscript. The range of ambient conditions for which the equilibrium model will give reliable results is

ACPD

4, S3561–S3565, 2004

largely dictated by the accuracy of the activity coefficient model. For the H+ - NH4+ - SO42- - NO3- - H2O inorganic model excluding Na+ and Cl-, Clegg et al (1998a) derived interaction parameters designed to make predictions over the temperature range $<$200K-330K. In ADDEM no ice or acid hydrate formation is treated, thus precluding its use for a range of upper tropospheric conditions where such species may be important. Having said that, studies have shown that mixed ambient aerosols remain aqueous at low RH and low temperatures (-10oC) (see Weingartner et al 2002 Env Sci Tech 36(1), 55-62 2002). For the organic model, the ability of UNIFAC to model systems of atmospheric importance has only been done at room temperature (ca. 298.15K) since data is severely lacking in the literature. The Dortmund UNIFAC model, though including a temperature dependence, was found to be particularly bad at modelling simple atmospheric systems (see figure 2). Thus the model can be considered reliable at a range of lower tropospheric conditions yet further proof is inhibited by a lack of data in the literature. Such is the case for other models available, and is not a problem specifically associated with ADDEM. This paper, using data available in the literature, along with other studies has shown that the additive approach for treating mixed inorganic/organic aerosols works well even down to low/moderate RH (ca. 40% RH), dependent on the liquid phase composition. Of course an uncoupled approach is expected to deviate from real behaviour at higher concentrations, though no better generalised technique is currently available.

P. 8685, l.5: ‘’Eq. 1’ should read ‘Eq. 3’’ Response - text altered accordingly

P. 8604, l.20: Write [P] instead of P. Response - text altered accordingly

P. 8696, l. 17: ‘Typo in reference ‘Sprow and Prausnit.m’’. Response-text changed to Sprow and Prausnitz

P. 86966: Eq (9) ‘what does symbol A_i mean?’ Response - in line 2, the definition of Ai which was missing has now been added ‘..,Ai the surface area of component ‘i’ in cm2 mol -1’.

ACPD

4, S3561–S3565, 2004

P. 8697, l.10: ‘Typo in ‘Sprow and Prausnit.m’’. Response-text changed to Sprow and Prausnitz

P. 8697, l.12: Symbol A should be in italics. Response - text has been changed.

P. 8698, l.17: It is Figure 8b instead of 8a that shows malic and maleic acid. Response - text has been changed.

P. 8699, l. 14/15: Skip text in parentheses. Response - text has been removed

Figure 2, Typo in the captions: ‘composition2’ is written twice. The second time it should read ‘Composition 3’. Response - text has been changed.

Figure 4 is not referred to in the text. Please add some comment or leave figure out. Response - This should have been referenced in section 2 ‘thermodynamics’. As such P8638 lines 20-24 have been modified to - ‘Whilst possible to include solid precipitation for the organic/water systems by using what little data is available to constrain the model, this is not treated here. Including solid precipitation within the modelling framework cannot be justified as the full range of interactions taking place is not considered (figure 4).’

Fig 6: the labels (a), (b), (c), (d) are missing. Response - the figures have been updated accordingly.

‘In three of the figures the molality is monotonic in increasing or decreasing with increasing RH whereas in the bottom right hand figure the dependence is oscillating. Is there an explanation for this behaviour?’ Response - Yes for this system ((NH4)2SO4 and organic acids) the data has been plotted to keep the RH increasing on the x-axis whereas the dry solute mole fraction oscillates (as given in the literature) thus producing the observed behaviour. If one looks at data for systems with the same dry solute mole fraction then one can see a decrease in molality as the RH increases.

‘The reference ‘marcolli et al ‘ is written in lower case twice’ Response - Figure captions have been updated to reference Marcolli rather than marcolli.

ACPD
4, S3561–S3565, 2004

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 8677, 2004.