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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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The authors would like to thank you for your time in reviewing this paper and support of the work which has been presented. The remarks made are addressed below.

Page 8678, line 18. Better to say "Ědeviations between model predictions and measurements increaseĚ". Response. Text has been updated accordingly. Line 18 now reads - 'As expected, deviations between model predictions and measurements increase with increasing concentration.'

Page 8692, line 21. Eq (4) should be introduced in the next line after it is mentioned - as opposed to at the end of the paragraph. Response - The body of text has been

rearranged to cover this issue.

Page 8692, line 24. Should it be Eq (4) instead of Eq (3)? Response - Yes, this has been pointed out by another referee and the text has been updated accordingly.

Page 8702, line 15-16 .'..at higher RH and lower dry size'. A preposition seems to be missing in this sentence. Response - line 15-16 now reads - 'Thus, the choice of surface tension model becomes more important for growth factor calculations as the RH increases and also as the dry diameter decreases.'

Is ADDEM able to predict deliquescence RH points of organics and mutual DRHs for mixed organic/inorganic systems? If so, then please show some examples and comparisons with available measurements (if any). Response - As discussed in the companion paper, ADDEM only requires energies of formation for treating solid precipitation. Thus it would be possible to include solid precipitation for single/mixed organic systems by using experimental data to constrain the model in the same way as the inorganic approach. The revised manuscript will briefly show this using a single organic compound and electro-dynamic balance data of [Peng et al., 2001]. Treating solid precipitation for mixed inorganic/organic systems is more difficult. As mentioned in the paper it is not treated here, purely from a theoretical standpoint, because the interaction between the inorganic/organic fractions are not dealt with. However, solids could be allowed to form in the separate inorganic and organic thermodynamic models. This has not been done because data seems to be lacking in the literature, or we are not aware of any available measurements. One could use HTDMA measurements for simple binary systems, however results in the literature often seem contradictory. There are additional problems with the latter approach such as the sensitivity to dry density and equilibration time compared with residence time in the humidifier.

Can the authors comment on how much error is expected in predicting water content and mutual DRHs of organic/inorganic mixtures considered in this study if activity coefficients for all the organic species are assumed unity or equal to their pure component

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(binary solution with water) values? The real question is that how important is it to accurately predict multi-component activity coefficients of various organics/inorganic mixtures? Response - This last question is particularly relevant to analysing our ability to model real atmospheric aerosols and one which the atmospheric science community as a whole would like to address. It is relatively easy to answer this in relation to only inorganic mixtures, and was addressed to some extent in the companion paper which highlighted the dangers of neglecting solute-solute interactions under conditions of low relative humidity. This also extended to the ability for treating solid precipitation. For more complex mixtures, including organics, one is hindered by a lack of experimental data and it is a difficult question to address at present. Including organic species in this discussion is difficult. Firstly, mutual DRHs of inorganic/organic mixtures were not considered in this study do to reasons addressed in the above response. However the study of [Marcolli et al., 2004], from which the mixture data was obtained, can provide some insight into the sensitivities involved in relation to assumed ideality. The authors calculated the MDRHs using only data from binary systems and found a maximum deviation of 2.5% RH compared to observations for the 5 component mixture of malic/malonic/maleic/glutaric/methysuccinic acid. However, one can also use calculations of saturation concentrations assuming ideality and then recalculate the mixture MDRH. In this report, it is possible to obtain the 'ideal' saturation concentrations for glutaric and malic acid. Using these values, the calculated MDRHS now deviate upto 11.92% RH for a mixture of malic and malonic acid) and 7.85% for the 5 component mixture (using only ideal data for two components). Thus, assumptions of ideality appear to introduce large erroneous results for this simple mixture. Similarly, [Clegg et al., 2001], using a coupled thermodynamic model and derived inorganic/organic interaction parameters, addressed this question to some extent by looking at systems for which experimental data is available. The authors found that for the sodium chloride/Sucrose/water system, a simplified approach to treating inorganic/organic interactions resulted in a 'satisfactory' reproduction of the deliquescence curve (see Clegg et al 2001). However, data was readily available for deriving mixed inorganic/organic inter-

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action parameters in this case. In calculations of the deliquescence properties for the letovicite/2-butanedioic acid/water system utilising different organic activity coefficient methods, differences in the predicted relative humidity over the eutectic mixture of 13% was identified; emphasising the importance of an accurate knowledge of the organic aqueous solution properties. It is unfortunately difficult to obtain a generalised error for a variety of systems Indeed, the study of [Peng and Chan, 2001] highlighted the need for a more accurate theoretical models in reproducing the water cycle of even simple organic species in the electrodynamic balance (which thus lead to a re-derivation of interaction parameters for use in the UNIFAC model). Such studies suggest that, at least in the sub-saturated humid regime, one cannot simply assume that all organic activity coefficients are unity. As mentioned in the paper, various studies on simple binary inorganic/organic systems have showed the ZSR approach to be adequate in modelling the water uptake (assuming the activity coefficient of organic species equal to those for a binary solution with water). Indeed, Marcolli et al (2004) found the ZSR approach to be adequate in modelling the mixed dicarboxylic acids presented in this paper. However, empirical data was not available for methylsuccinic acid and the authors assumed an uptake behaviour equal to that of glutaric acid, thus preventing a comparison with a full thermodynamic treatment in this paper. Thus it is difficult to extrapolate predictive uncertainties to more complex mixtures at the present time. However, using models such as ADDEM it is possible to explore the range of conditions for which significant differences exist between this approach and more simplified techniques. Indeed, this will be the focus of future work.

Bibliography

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