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Atmospheric Chemistry and Physics Discussions

# *Interactive comment on* "Mass-based hygroscopicity parameter interaction model and measurement of atmospheric aerosol water uptake" *by* E. Mikhailov et al.

**Anonymous Referee #3**

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Manuscript overview

This manuscript by Mikhailov et al. entitled 'Mass-based hygroscopicity parameter interaction model and measurement of atmospheric aerosol water uptake' discusses mass-based kappa theory, and applies it to the field data. The topic of the manuscript is relevant to the journal. The reviewer thinks that further clarification would be required prior to publication in ACP.

Major comments

It is not clear why the development of a new theory is required. The authors state that 'For the reasons outlined above (mass conservation vs. volume non-additivity) the



more detailed solute interaction models are generally also mass based rather than volume based (P30890L20).' The reviewer totally agrees with this statement. In that case, it seems more reasonable to expand those available models so that they can also be applied to complex systems such as atmospheric aerosols, as it enables to incorporate the output of those existing models into the data analysis directly. The reviewer personally concerns that introduction of many 'novel' parameters for one phenomenon is going to introduce confusions to the field. The reviewer would like to ask the authors to add a sufficient explanation to demonstrate the reasons why it is required to develop the mass-based kappa-theory.

Specific comments

P30878L20 'gradual deliquescence'

'Deliquescence' indicates an abrupt change. Therefore, this term includes two contradicting ideas. Other terms such as 'gradual dissolution' (if this is what the authors mean) may be more appropriate.

P30879L6 'critical diameters'

As far as the reviewer's knowledge, this technical term is commonly defined as droplet diameter corresponding to critical supersaturation. It is preferred to call this diameter as 'critical dry diameter' or 'critical dry activation diameter' to avoid confusion.

P30879L7 "The application of KIM and mass-based measurement techniques shall help to bridge gaps in the current understanding of water uptake by atmospheric aerosols: (1) the gap between hygroscopicity parameters determined by HTDMA (hygroscopicity tandem differential mobility analyzer) or FDHA measurements under subsaturated conditions and by CCN measurements at water vapor supersaturation, and (2) the gap between the results of simplified single parameter models widely used in atmospheric or climate science and the results of complex multi-parameter ion- and molecule-interaction models frequently used in physical chemistry and thermodynam-

ics (AIM, E-AIM, UNIFAC, AIOMFAC etc.)."

It was not clear how this goal was (will be) achieved, even after reading the whole part of the manuscript. A detailed description on the strategy to achieve this goal is required.

P30882L18 'Depending on aerosol particle sources and properties, the deviations from ideality can range from a few percent up to a factor of 2 or more.'

Is it possible to show some examples that the deviations from ideality exceed a factor of 2?

P30883L7 'dilute intrinsic hygroscopicity kappai,$\infty$'

This term is ambiguous. If this word indicates 'solution concentration corresponding to critical supersaturation', the sign of '$\infty$' should not be used because properties of solutions at the corresponding concentration range are significantly different from those of infinitely dilute solutions. If this word really means 'kappa value at infinitely dilute condition', the following statement in the concluding section would not be accurate for the same reason. 'The parameter k6 determined by fitting of Eq. (34) to hygroscopic growth data obtained in the dilute regime at high humidity represents the dilute intrinsic hygroscopicity of the aerosol (kappai,$\infty$) and can be used to predict CCN activation diameters as a function of water vapor supersaturation'

P30883L19 'where d is the effective density of the dry particle material'

Effective density is normally defined as a ratio of particle mass and apparent particle volume (e.g., particle volume estimated from mobility diameter), assuming that particles are spherical. This includes the material density of particles as well as non-sphericity. On the other hand, material density is the ratio of actual mass and actual volume (i.e., it does not include any information on particle shape). It is not clear if this statement refers to effective density or material density.

P30888Equation20



Is it possible to explain the reasons why those interaction terms are second-order with respect to concentration in more detail? It is not clear how this formulation is compared with other methods such as AIM and UNIFAC.

P30891Section3.1

The reviewer is wondering if the authors also did experiments on pure ammonium sulfate particles. Sulfate ion is +2, therefore Debye-Hückel effect for ammonium sulfate solution is more significant than that for sodium chloride. It makes the magnitude of non-ideality of the solution larger, and hence, it would serve as a better test for the capability of mass-based kappa theory (i.e., The reviewer is not sure if the KIM model works well for ammonium sulfate, even if it provides a reasonable result for sodium chloride).

P30893L15' The observation of a transition range rather than a sharp threshold value of RH can be explained by inhomogeneities and polydispersity of the investigated particles, whereby larger particles are likely to effloresce at higher RH.'

Particles on filter may have capillary condensation in between the filter fibers and particles. The reviewer is wondering if this affects the measurement.

L30898L10 'The steep slope reflects a high value of the fit parameter k6, which in turn indicates strong interaction between the organic solute molecules in the AMAZE sample (Eq. 40, Table 3).'

It would be ideal to have a description explaining the reason why the contribution of inorganic species can be ignored.

L30898L15 'Most likely the more prolonged concentration effect for the AMAZE particles arises from a high content of the sparingly soluble compounds'

It is not clear why other possibilities such as the difference in non-ideality and different inorganic mass fraction can be ruled out. Further description is required.

Figure 4

The panel for NaCl particles is very confusing. Various experimental data are cited in this panel. However, it is not clear if NaCl is used to calibrate the instruments or if it is measured after calibrating the instruments using other chemical species such as ammonium sulfate. In addition, it is not clear if those critical dry diameters are corrected for shape factors. A further description needs to be added to explain this figure.

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Interactive comment on Atmos. Chem. Phys. Discuss., 11, 30877, 2011.