

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

Anonymous Referee #1

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In this manuscript an approach for description of water uptake by atmospheric aerosol particles using a mass-based hygroscopicity parameter is presented and an interaction model KIM is developed. This interaction model is applied to FDHA (filter-based differential hygroscopicity analysis) measurements of NaCl filter samples and filter samples from the AMAZE (Amazon) and SPB (Saint-Petersburg) campaigns. The NaCl and AMAZE samples are compared with CCN activation derived kappa values. The work in this paper is well presented, nevertheless, the authors fail to convince why the KIM interaction model is needed at all. To describe the water uptake of the samples, new nomenclature is introduced that seems intuitive, but is, when giving it a closer look, not well defined and confusing. These issues have to be resolved before the manuscript

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can be published in ACP.

KIM interaction model

In section 2.3 the “Hygroscopicity parameter interaction model (KIM) is developed. Eq. (22) gives the general expression that is simplified to Eqs. (25 – 28) depending on the phase state of the system. However, even these simplified expressions cannot be applied to an atmospheric sample as is stated in section 4.2. Eqs. (32-40) give therefore a further simplification. With this simplification, it is possible to derive mass-based hygroscopicity parameters from the FDHA data. To do this, three different regimes are discriminated:

Regime I (quasi-eutonic): The authors use the expression “quasi-eutonic” without defining it. In the abstract, they claim that in this “quasi-eutonic regime” “the solutes co-exist in an aqueous and non-aqueous phase”. However, they do not further explain the nature of these two phases. If we replaced “quasi-eutonic” by “eutonic” the situation would be clear: there would be multiple crystalline solid phases below the eutonic RH of the mixture (giving a conglomerate of non-aqueous phases) but no aqueous phase. An aqueous phase would only appear at the eutonic RH. In the “quasi-eutonic” regime an aqueous phase and only one non-aqueous phase are claimed to co-exist at low RH. The authors might have a (semi)solid amorphous phase in mind. If so, this should be explicitly discussed. However, in this case, the notion that each solute has its own saturation solubility is not applicable anymore.

Regime II (gradually deliquescent): In the abstract the authors claim that in this regime, the “solutes undergo gradual dissolution in the aqueous phase”. However, when the aqueous phase was already present in regime I, there must have been gradual dissolution already in the first regime and the difference between the two regimes becomes unclear.

Regime III (dilute): in this regime, the solutes are fully dissolved.

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Discrimination between the three regimes as outlined in the manuscript is therefore not justified. Also, a full fit of hygroscopicity parameters for all three regimes is not needed to predict CCN activation diameters because for this, only the dilute intrinsic hygroscopicity of the aerosol is relevant (as stated e.g. in the summary and conclusion, page 30900, lines 25 – 28.), which can be derived using Eq. (34) of the KIM model. Figure 4b indeed shows that the KIM model leads to an accurate prediction of critical dry diameter for CCN activation of the AMAZE sample. However, the simpler procedure by evaluating the mass based hygroscopicity parameter at a high RH (e.g. at 90 %RH as in Carrico et al., 2010, or at 95 %RH as in Duplissy et al., 2008) might do as well and the complex KIM model would be not needed at all. If this is the case, additional examples should be presented for which the use of the KIM model is really an advantage or this model should be omitted in the final version of the manuscript.

Nomenclature

Throughout the manuscript the use of nomenclature is confusing and must be improved. The supposed phase composition during hygroscopic growth should be more explicitly discussed. Below are some examples where improvement is needed:

Page 30882, line 18: what is meant in this context with “ideality”?

Page 30883, line 19: what is the definition of “effective density”? How can it be determined?

Page 30888, line 12: what is meant with an aqueous phase: an aqueous liquid phase? What is meant with a non-aqueous phase: a crystalline solid phase? A conglomerate of crystalline solid phases? An amorphous water-free phase?

Page 30889: lines 17 – 18: I do not understand this sentence: in what phase state should the substances co-exist in the non-aqueous phase? Co-existence of crystalline solid phases and an aqueous phase for which the concentration of each component corresponds to the eutonic solubility occur at the eutonic RH only. Do the authors refer

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to exactly this RH?

Page 30895, lines 12 – 14: What is meant with “quasi-eutonic conditions”? What is meant with “a non-aqueous state”? What is meant with “effective eutonic solubilities”?

Page 30897, line 20: what is meant with “quasi-eutonic RH”?

More specific comments:

Page 30882, Eq. 5: it should be mentioned that this equation assumes solution ideality.

Page 30884, lines 15 – 23: Do the authors consider the conversion of volume-based to mass-based hygroscopicity parameters as a problem? The reasoning in the paragraph from line 15 – 21 seems to say “yes”. The next paragraph seems to say “no”.

Page 30885, Eqs. 13 – 15: Derivation of these equations should be given in an appendix or supplementary material.

Page 30891, Table 2: was there only one filter sample collected during the whole sampling period?

Page 30892, lines 10 – 11: how was the sample mass on the cut out filter aliquot determined?

Page 30898, line 6: 2-methyltetrols are a bad example of sparingly soluble SOA. They are well soluble in water.

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