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

We would like to thank Referee #1 for the constructive criticism and suggestions for improvement that were taken into account upon manuscript revision. Responses to individual comments are given below.

General comments:

Comment

The work in this paper is well presented, nevertheless, the authors fail to convince why the KIM interaction model is needed at all.

Response

For a detailed answer to this comment we refer to the authors’ general comments in the public discussion of ACP.

Comment

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.

Response

The term “eutonic solubility” normally refers to a liquid phase in stable equilibrium with multiple crystalline phases. Partly dissolved solutes may also co-exist in meta-stable equilibrium with amorphous phases. For this “quasi-eutonic” state, the maximum aqueous phase concentrations of a solute can be characterized by an apparent solubility, $C_{m,i}^{ap}$, replacing the eutonic solubility $C_{m,e,i}$ in Eq.(26). Apparent solubilities are well-established parameters for the description of the water interactions of amorphous substances as discussed below and in the scientific literature dealing with semi-solid or solid amorphous organics in the pharmaceutical and food sciences (Mosharraf et al, 1999, Hancock and Parks, 2000; Murdande et al., 2010; 2011). In contrast to the thermodynamically fixed value of equilibrium solubility, however, the apparent solubility of a substance is a kinetically limited parameter that may vary depending on the pre-treatment and history of the investigated system. The apparent solubility enhancement ratio $R_{ap,i} = C_{m,i}^{ap} / C_{m,i}$ can be used to describe the degree of supersaturation and meta-stability of the system (Hancock and Parks, 2000; Murdande et al., 2010; 2011).
In the revised manuscript we added this comment below Eq. (26).

Comment

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. 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.

Response

The difference between regime I (quasi-eutonic), regime II (gradual deliquescence), and regime III (dilute) is a corollary of the theory model, which describes three typical stages of mixed particle evolution in water vapor (Eqs.23; 26 and 27). In the "quasi-eutonic regime", the linear increase (decrease) of κ_m with G_m can be described by Eq. (26), assuming quasi-eutonic conditions where the solutes co-exist in partly dissolved state. In the "gradual deliquescence" regime at intermediate humidity where different solutes undergo gradual dissolution or solidification in the aqueous phase the dependence of κ_m on G_m can be described by Eq. (23), In the "dilution regime", where the solutes are fully dissolved the dependence of κ_m on G_m can be described by Eq. (27).

The KIM was generally built to describe water uptake at low RH (see the authors' general comments). This is particularly important for direct aerosol forcing modeling. Prediction of CCN properties of mixed particles is only a special case of the proposed model, which in turn is important for indirect aerosol forcing modeling. As shown in the text (p.30898, line 21) only one dilute hygroscopicity parameter, $\kappa_{m,\infty}$ (κ_m^0 in the updated manuscript) obtained in the dilution mode was used to predict CCN activation. The results presented in chapter 4.3 (4.6 in the updated manuscript) just demonstrate that among the description of the water uptake at low RH the KIM model can also be used for prediction of the CCN activation.

To verify the model efficiency, in the revised manuscript, new substances have been included and the modeling results were compared with E-AIM and E-ZSR models. New compounds are: ammonium sulfate (AS), levoglucosan, malonic acid (MA), and AS-MA with 1:1 mole. In addition CCN predicted dry activation diameters for AS particles are also presented. Testing results have shown that KIM provides a good agreement for all listed species, and the obtained quantities of the fit parameters have reasonable physical interpretation (see also Author's general comment).

Specific comments: Nomenclature

Comment

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:

Response

The nomenclature has been revised as detailed below and in the manuscript (text and list of symbols).

Comment

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

Response

As described in the referenced studies, the mobility equivalent diameters of porous and irregularly shaped particles can be up to a factor of 2 larger than the volume or mass equivalent diameters, which implies deviations up to a factor of eight in effective particle density (Krämer et al., 2000). To avoid confusion about the meaning of ideality in this context (sphericity, compactness/density), we removed the above sentence from the revised manuscript.

Comment

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

Response

We have replaced this wording as follows " … ρ_d is the density of the dry particle material".

Comment

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?

Response

For clarity we have replaced the terms "aqueous liquid phase (aq)" and "non-aqueous phase (na)" by "fully dissolved (fd)" and "partly dissolved (pd)", respectively.

Comment

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 to exactly this RH?

Response

The sentence on Page 30889, lines 17 – 18 will be reworded as follows: "If all substances are just partly dissolved (pd) and exist also in a non-dissolved phase, the concentration of each component is given by the eutonic solubility, $C_{m,i}^{eu}$.

Comment

Page 30895, lines12 – 14: What is meant with "quasi-eutonic conditions"? What is meant with "a non-aqueous state"? What is meant with "effective eutonic solubilitites"? Page 30897, line 20: what is meant with "quasi-eutonic RH"?

Response

These items have already been discussed above. The determination of the quasi-eutonic state and the effective (apparent) eutonic solubility will be presented in the revised manuscript.

More specific comments:

Comment

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

Response

In Eq.(5) the κ-hygroscopicity parameter is determined as "effective Raoult parameter" (line 3, page 30883), which is equivalent of an ideal solution. Further clarification regarding this parameter is given in lines 5-10 on page 30883.

Comment

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".

Response

For the reasons discussed in the manuscript (mass additivity versus volume additivity) the conversion of mass water uptake measurements (κ_m) into volume basis (κ_V) can be done on the condition that the volume additivity rule is valid. This becomes possible at a high RH when interaction effects are negligibly small and the KIM model transforms into an analog of the regular κ_V - hygroscopicity model (Eq. 17; Eq.7) (Petters et al., 2007).
To avoid confusion, in the revised manuscript it is noted that volume additivity has to be assumed for Eq. (7).

Comment

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

Response

The derivation of Eqs.13-15 will be presented in the Appendix B of the revised manuscript.

Comment

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

Response

Yes, only one filter sample was taken during the whole sampling period, but 4-5 circular aliquots were available for water uptake measurements.

Comment
Page 30892, lines 10 – 11: how was the sample mass on the cut out filter aliquot determined?
Response
The sample mass was calculated based on the aerosol mass loaded on the filter (47 mm) and the ratio between the mass loaded area of the circular aliquot (13 mm) and the mass loaded area of the original filter (42 mm).

Comment
Page 30898, line 6: 2-methyltetrols are a bad example of sparingly soluble SOA. They are well soluble in water.
Response
The sentence on P.30898, lines 3-7 has been removed.

References:

Hancock, B. C., and Parks, M.: What is the true solubility advantage for amorphous pharmaceuticals?, Pharm. Res., 17(4), 397-404, 2000.

Krämer, L., Pöschl, U., and Niessner, R.: Microstructural rearrangement of sodium chloride condensation aerosol particles on interaction with water vapor, J. Aerosol. Sci., 31, 6, 673-685, doi:10.1016/S0021-8502(99)00551-0, 2000.

Mosharraf, M., and Nyström, C.: The effect of dry mixing on the apparent solubility of hydrophobic, sparingly soluble drugs, Europ. J. Pharm. Sci., 9, 145-156, 1999.

Murdande, S. B., Pikal, M. J., Shanker, R. M., and Bogner, R. H.: Solubility advantage of amorphous pharmaceuticals, II. Application of quantitative thermodynamic relationships for prediction of solubility enhancement in structurally diverse insoluble pharmaceuticals, Pharm. Res., 27, 2704–2714, 2010.

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