

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 #3 for the remarks and constructive comments, which will be taken into account upon manuscript revision. Responses to individual comments are given below.

Major comment

It is not clear why the development of a new theory is required.

Response

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

Specific comments:

Comment

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.

Response

In our earlier paper (Mikhailov et al., 2009) we proposed not to limit the terms deliquescence and efflorescence to equilibrium phase transitions of crystalline substances (salts) interacting with water vapor. Instead we proposed the following generalized definitions:

- a) Deliquescence is the transformation of a (semi-)solid substance into a liquid aqueous solution, whereby water is absorbed from the gas phase (“liquefaction/ liquescence upon humidification/hydration”).
- b) Efflorescence is the transformation of a substance from a liquid aqueous solution into a (semi-)solid phase, whereby water is evaporated (“solidification upon drying/ dehydration”).

According to these definitions, individual components as well as entire aerosol particles can undergo gradual or prompt, partial or full deliquescence or efflorescence, which is indeed the case not only for amorphous organic substances but also for mixtures of crystalline inorganic substances.

The broad definitions of deliquescence and efflorescence proposed above are consistent with the definition proposed by IUPAC (<http://goldbook.iupac.org/D01582.html>) and the various definitions used throughout chemistry, biology and medicine, which are usually not restricted to crystalline substances (e.g.:

<http://www.merriam-webster.com/dictionary/deliquescence>, <http://www.biology-online.org/dictionary/Deliquescence>, <http://medical.merriam-webster.com/medical/deliquesce>, <http://chemistry.about.com/od/chemistryglossary/a/deliquescencedf.htm> , etc.).

Note that earlier studies have already used the term deliquescence in ways that go beyond classical equilibrium phase transitions and deliquescence points. Thus the term “deliquescence curve” (i.e. gradual deliquescence) is often used in thermodynamic models to describe phase equilibrium of the mixed systems by Clegg et al. (2001, 2004,

2006). See also discussions of pre-deliqescence and non-prompt, nucleated or other pathways of deliquescence (e.g., Cantrell et al., 2002; Biskos et al., 2006; Zardini et al., 2008; McGraw and Lewis, 2009, and references therein).

Comment

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.

Response

The term “critical diameter” will be replaced by “dry diameter of CCN activation”.

Comment

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 thermodynamics (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.

Response

Since the hygroscopicity parameter is concentration dependent the HTDMA-derived κ and CCN-derived κ are systematically different to each other (Petters and Kreidenweis, 2007; Mikhailov et al., 2009). The proposed κ_m – hygroscopicity interaction model (KIM) is able to describe concentration dependence and therefore bridge the gap in understanding the water uptake by aerosol particles in sub- and super-saturated conditions. As a consequence the KIM can reproduce both the characteristics of water uptake under subsaturated conditions and predict correctly their CCN properties.

The KIM also is a “bridge” between simplistic assumption of a constant single κ -model and more complex multi-parameter thermodynamic models. The Eqs. (28), (29) and Eq.(30) (Eq. 31 in the revised manuscript) are trivial examples of this bridge.

To verify the model efficiency, in the revised manuscript, we included new substances and compared the modeling results with E-AIM, E-ZSR, and UNIFAC. The added 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 that the obtained quantities of the fit parameters have reasonable physical interpretation.

Additional comments on the considered issue are given in the authors’ general comments.

Comment

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?

Response

As described in the referenced studies, the mobility equivalent diameters of porous and irregularly shaped particles can be by up to a factor of 2 larger than the volume or mass equivalent diameters. This 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

P30883L7 *‘dilute intrinsic hygroscopicity kappa ‘∞’*

This term is ambiguous. If this word indicates ‘solution concentration corresponding to critical supersaturation’, the sign of ‘∞’ 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 κ_6 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 ($\kappa_{p,i}$) and can be used to predict CCN activation diameters as a function of water vapor supersaturation’

Response

The symbol “∞” is associated with the conceptual framework of the hygroscopicity interaction model (KIM) and does not directly indicate “*solution concentration corresponding to critical supersaturation*”. According to Eq. (27) or Eq. (29), when G_m goes to infinity (“∞”) the particle solution is infinitely diluted and the dilute hygroscopicity, κ_∞ becomes constant (Eq.17). It means that interactions between solute ions and molecules are negligibly small. In most cases, these conditions are well justified for the CCN activation of aerosol particles. Therefore the experimentally derived κ_∞ (Table 4) have been used to predict the dry particle activation diameters based on the κ_m -Köhler model (Eq.12).

For clarity the symbol “∞” has been replaced by “0” everywhere in the revised manuscript.

Comment

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 nonsphericity. 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.

Response

We have removed “effective” from the determination of the density: “... ρ_d is the density of the dry particle material”.

Comment

P30888 Equation20

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.

Response

We consider incremental hygroscopicity terms $\delta\kappa_{m,ij}$ (Eq.20) as a product of binary interaction between different species, which are then summed. The probability of interaction (interaction strength) between two species is proportional to the concentration of each of the two. Therefore, interaction terms are second-order with respect to concentration. The same order relative to concentration is used in thermodynamic and extended ZSR models. That is the second order for binary interactions, the third order for ternary interaction and so on (see, for example Eqs. (6, 7a-c) in Clegg et al., 2001; Eq. (7) in Clegg et al., 2004).

The comparison of the KIM with E-AIM and E-ZSR models is given in Appendix B of the revised manuscript.

Comment

P30891 Section3.1

The reviewer is wondering if the authors also did experiments on pure ammonium sulfate particles. Sulfate ion is +2, therefore Debye-Huckel 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).

Response

The KIM modeling results for ammonium sulfate are in agreement both with experimental and rigorous AIM and is shown in Fig. 2b of the revised paper.

Comment

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.

Response

The Filter-based Differential Hygroscopicity Analyzer (FDHA) (*Izvestiya, Atmospheric and Oceanic Physics*, 2011, Vol. 47, No. 6, pp. 747–759 (<http://www.springerlink.com/content/m63203237157248g/>)), which we used for the measurement of mass water uptake at different RH consists of two cells. A filter ($D=13\text{mm}$) with aerosol particles is placed inside the measuring cell, and a pure filter is placed in the comparison cell. Vapor is absorbed by walls and filter surfaces in both cells;

it is additionally absorbed by aerosol particles in the measuring cell. The difference in the concentrations of water molecules in the flows passing through the measuring and comparison cell is detected with a differential sensor. Thus, the potential capillary condensation on the fibers is subtracted. A good agreement between FDHA-measured water uptake with AIM confirms that capillary condensation between the fibers and aerosols is beyond the sensitivity of this method even at 99% RH. Moreover we have tested tissuquartz and fiber glass Teflon coated filters to estimate capillary effects and did not find any difference.

We also conducted additional FDHA measurements with size selected ammonium sulfate and sodium chloride particles. These data demonstrate stepwise deliquescence and efflorescence transitions. Moreover the water uptake FDHA results are identical to these obtained by a single particle levitation method and are in excellent agreement with thermodynamic AIM (see updated Fig. 2a and Fig. 2b).

Comment

P30898L10 “The steep slope reflects a high value of the fit parameter k_6 , 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.

P30898L15 “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.

Response

The statements were meant to provide a tentative explanation for the observed differences between the investigated samples, but we did not intend to rule out potential other effects and/or alternative explanations. A more thorough investigation of the differences would go beyond the scope of this manuscript. The formulation has been therefore removed in the revised text to avoid over interpretation or misunderstandings.

Comment

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.

Response

As stated in the introductory sentence (30898 L19), the section 4.3 is devoted to test the applicability of the mass-based hygroscopicity parameter interaction model for predicting CCN activity based on subsaturated FDHA data (Fig.4a (revised Fig.7a)) just shows the predicted dry activation diameters for NaCl particles based on KIM and FDHA measurements. Independent experimental and theory results are shown to compare the quality of the prediction. The FDHA method does not require external calibration. Moreover the method is based on mass water uptake and therefore it needs no correction for the shape factor. This section has been also extended in the revised manuscript with KIM predicting the CCN properties of ammonium sulfate particles (Fig.7b).

References

Biskos, G., Paulsen, D., Russell, L. M., Buseck, P. R., and Martin, S.T.: Prompt deliquescence and efflorescence of aerosol nanoparticles, *Atmos. Chem. Phys.*, 6, 4633–4642, 2006.

Cantrell, W., McCrory, C., and Ewing, G.: Nucleated deliquescence of salt. *J. Chem. Phys.*, 116, 2116-2120, 2002.

Clegg, S. L., Seinfeld, J. H., and Brimblecombe, P.: Thermodynamic modelling of aqueous aerosols containing electrolytes and dissolved organic compounds, *Aerosol Sci.*, 32, 6, 713-738, doi:10.1016/S0021-8502(00)00105-1, 2001.

Clegg, S. L., and Seinfeld, J. H.: Improvement of the Zdanovskii-Stokes-Robinson model for mixtures containing solutes of different charge types, *J. Phys. Chem. A*, 108, 1008-1017, 2004.

Clegg, S. L., and Seinfeld, J. H.: Thermodynamic models of aqueous solutions containing inorganic electrolytes and dicarboxylic Acids at 298.15 K. 1. The acids as nondissociating components, *J. Phys. Chem. A.*, 110, 5692-5717, 2006.

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.

McGraw, R., and Lewis E. R.: Deliquescence and efflorescence of small particles, *J. Chem. Phys.*, 131, 194705, 2009.

Mikhailov, E., Vlasenko, S., Martin, S. T., Koop, T., and Pöschl, U.: Amorphous and crystalline aerosol particles interacting with water vapor: conceptual framework and experimental evidence for restructuring, phase transitions and kinetic limitations, *Atmos. Chem. Phys.*, 9, 9491-9522, doi:10.5194/acp-9-9491-2009, 2009.

Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, *Atmos. Chem. Phys.*, 7, 1961-1971, doi:10.5194/acp-7-1961-2007, 2007.

Zardini, A. A., Sjogren, S., Marcolli, C., Krieger, U. K., Gysel, M., Weingartner, E., Baltensperger, U., and Peter, T.: A combined particle trap/HTDMA hygroscopicity study of mixed inorganic/organic aerosol particles, *Atmos. Chem. Phys.*, 8, 5589-5601, doi:10.5194/acp-8-5589-2008, 2008.