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Atmospheric
Chemistry
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Discussions

Interactive comment on "Aerosol hygroscopic growth parameterization based on a solute specific coefficient" *by* S. Metzger et al.

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The authors present a parameterization of aerosol water contents that can be applied to either compute the water activities of bulk solutions or, with additional terms in the equations, be used to compute water contents as a function of particle dry diameter. The parameterizations are potentially useful if they can be shown to be more accurate than existing formulations, while remaining computationally efficient.

In the following, I will address only one aspect of the presented work, namely the parameterization of bulk water activity as this comparison is more straightforward than those involving the Kelvin term, which depends in turn on the choice of dry diameter. The relevant equation for this special case is equation 17c, which truly is a single-parameter equation.

The applicability of the PK2007 parameterization below water saturation (also evaluated, as done here, by comparing with the AIM model) was explored by Kreidenweis et al. (2008) [Kreidenweis, S.M., Petters, M.D., and DeMott, P.J., Single parameter estimates of aerosol water content, Environ. Res. Lett., 3, 035002, doi:10.1088/1748-9326/3/3/035002, 2008; the authors should add this article to their references as it is directly relevant to this paper]. SPD2008 showed that appropriate choices of kappa could generally represent the subsaturated aerosol water contents within 20%, except for sodium salts. For the sodium salts studied, the (a_w/(1-aw)) function simply does not well represent the actual functional dependency. Thus I was particularly interested in the application of the proposed parameterization to NaCl.

In the Addendum to this review I show a comparison between the present parameterization, using Equation 17c and the recommended parameters for NaCl and ammonium sulfate, and the PK2007 formula using the kappa values recommended in SPD2008. Following SPD2008, the comparisons are shown in terms of the volume of water per volume of dry solute, since accurate water contents are of interest. The authors' parameterization does a nice job of representing the water contents for NaCl, much better than PK2007, and the fit for ammonium sulfate is also very good and similar to PK2007 over a wide range of water activities.

This comparison thus demonstrates the potential utility of the new single-parameter equation (17c) in modeling water contents of atmospheric aerosol. I would recommend that the authors remove some of the superfluous review material at the beginning of their chapter, and present the form and results of the (bulk solution) water activity fits in a more straightforward way so they can be appreciated by a wider audience. In the present form of the manuscript it is very difficult to understand the magnitude of the differences between the various formulas used to create the HGF figures.

My second comment concerns the other equations presented for computing water contents (17a, 17b, 17d). If I understand correctly, in order to compute the A and B parameters, one needs not only the solute-dependent "single parameter" nu_i, but an

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additional piece of information that is stored for the solute under question, for example the value of molality at saturation. Thus all of the remaining equations become multi-parameter, and not single-parameter, fits; this is seen explicitly in 17d, where a new parameter B_98 is introduced. Of course any fit to data or to AIM model output can be made much better with additional fitting parameters, and it is not surprising that they are needed to capture solution nonidealities. However, the Abstract must be modified so as not to give the impression that a single parameter is adequate over the entire range of solute composition.

A third point regards the handling of mixtures of solutes. Most thermodynamic models assume the applicability of the ZSR relation, which states that water contents of binary solutions can be added to estimate the water content of the mixture. Certainly the single-salt parameterizations proposed here could be computed individually and then the water contents added in the same way. The unique advantage of the PK2007 parameterization arises because the same functional dependence on a_w is used for all solutes, and then it can be shown that the ZSR assumption is equivalent to volume weighting the kappas of the mixture components one performing ONE calculation for the mixed-solute water content. This is not possible with the proposed parameterization because the functional dependence on a_w changes with each solute.

Again, as with any parameterization, there is a tradeoff between accuracy and computational efficiency. The PK2007 parameterization is very simple and so far appears to work well for water contents at high water activities, such as those accessed during droplet nucleation. However, it is poor in the subsaturated regime for sodium salts, and certainly should not be applied under those conditions without corrections.

The parameterizations proposed here can likely be shown to be superior for some solutes and over some ranges of water activity. The comparisons to other formulas, however, should be made “apples to apples”, that is, single-parameter fits can be compared to each other, and multi-parameter fits need to be clearly identified and their improvements quantified. As pointed out by other reviewers, if computational efficiency

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over other methods is to be stressed, then appropriate metrics should be presented.

The parameterization presented here is designed to be implemented in EQSAM4, and so I appreciate that the authors wish to have it documented in the literature and its behavior with respect to a standard (here, AIM) demonstrated. The formulas presented here certainly have merit in representing aerosol water contents and merit publication, although again I recommend that the presentation be revised so that a larger audience can understand how they fit in to the larger picture of how aerosol water contents have been computed in models. In my review I have focused only on one part of the presented parameterization, the bulk solution water contents, which are key to the accurate representation of the equilibrium expressed in equation 1. However, the authors' point is a good one, in that inaccuracies in the computation of (bulk) water content feed back into the calculation of the wet diameter, and thus can result in errors in the magnitude of the Kelvin term. It is of interest to quantify those feedbacks; I would suggest to separate the bulk solution fits from those considering particle size and to demonstrate the individual contributions to error. Further, the authors present additional equations for dealing with the variations in dry particle diameter, which are presumably important in their model application. These seem complicated to introduce into a model that deals with an entire distribution of particle sizes, and perhaps more guidance can be given on how this is done in the model (e.g., using a fixed number of bins?) and what uncertainties are introduced compared with, e.g., accurate water contents for a full lognormal distribution.

The Abstract should be revised in accordance with these comments and with the revisions that are made to the manuscript.

Minor points:

p. 24815, line 16: this statement is incorrect. There are species (e.g., organic molecules) capable of forming aqueous solutions that are not ionic. For example, sucrose has a rather high kappa value.

bottom of page 24816-top of page 24817: The f(RH) method can actually be used to include effects of deliquescence. Since the observed behavior is merely fit to convenient equations, there is not really any theoretical limitation to how complex the fits are made. Further, some effects that occur in “real” aerosols may be implicitly captured in the observations.

bottom of page 24818, lines 13 on: I would argue that the identification of terms as “Raoult” and “surface” terms confuses the issue since they arise from the simplified (classic) Kohler equation which does not apply over the full range of water contents. I would recommend, as noted above, to separate out the water activity term and the Kelvin term and discuss their contributions to water content separately.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/11/C11479/2011/acpd-11-C11479-2011-supplement.pdf

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