

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

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Reply to R. Lescroart

We thank R. Lescroart for his Interactive Comment.

We hope to have clarified the issues raised and satisfactorily addressed all comments with the point-to-point reply below. The suggested corrections and additions will be included in the revised manuscript.

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Interactive Discussion

Discussion Paper

Apart from a lot of long known theoretical considerations, and a review on (5 ?) water activity representations (from line 15, p. 24819 to line 21, p.24823), this paper is without much scientific content. The parameterization equations (equations 15, 16a to (20)) do not content better information than the experimental or model curves they are drawn from. The newly found "single solute specific coefficient" ν_i has no specific physical meaning or gives no better physical insight. According to the authors' findings, it could be considered as a solute specific constant (lines 14 p.24814, and 7 and 21 p.24824). So, the interest must be elsewhere.

We respectfully disagree. The theoretical considerations (Sect. 2.1.1) are essential as they provide the context in which the ν_i -method is to be evaluated. And within this context the ν_i -method is more accurate than the other single parameter formulation for concentrated solutions. The single solute specific coefficient ν_i gives insight similar to any other parameterization coefficient mentioned in Sect. 2.1.1, e.g. the κ -method (p24821), i.e. it helps to predict water uptake with extraordinary accuracy with regional and global models. Since the ν_i -method outperforms the κ -method for concentrated NaCl solutions as shown also by the Addendum of S. Kreidenweis (Referee) and our figures 3 and 4 – our work deserves publication in ACP.

Scientific progress: Our empirical single parameter equation allows to cover the complete range of the Köhler-curve from concentrated solution up to high dilution beyond the critical supersaturation. We suggest a simple method to determine our parameter ν_i ; as we have shown, it can be easily determined at the point of deliquescence with our equation. Afterwards it is kept constant for the entire RH, μ_s -range covered by the Köhler-curve. Furthermore our parametrization applies to both single and multi-charged solutions. As far as we aware of, this is the first single parameter equation with such a capability. We show that our results are in good agreement with comprehensive state of the art aerosol thermodynamics modeling.

Physical insight: Our empirical approach describes the water activity based on a function of type $a_w \approx 1/(\nu_i[\mu_s]^{\nu_i})$. Even though it is empirical, why could it not also have physical implications? We have shown that a single parameter description for the complete Köhler-curve exists. Since our findings are empirical we can't and we don't state that this is the only (or simplest) possible single parameter equation. But it can be argued that the sheer fact of its existence puts a kind of constraint on explicit comprehensive physical aerosol models. The fact that the combined effects of the molecular driving forces (which might be quite complex) responsible for aerosol water uptake (Köhler-curve) can be described to a good approximation by a single parameter function, and that this single parameter can be determined at the point of deliquescence and stays constant is noteworthy.

The authors want to introduce a new and simpler parameterization for the water activity in function of the solute molality. The problem is that this relation depends on ν_i and two other functions (or best fittings (line 13 p 24827) A and B (equations (18 to (20)) themselves depending on ν_i . The solution proposed by the authors themselves (lines 12 to 19, page 24828) is to start with the molality and water activity "at saturation" to determine A and B. And afterwards to use these values to determine ν_i . The problem is they don't have a starting value for ν_i and so, in their own scheme, they can't calculate A or B. This won't work.

We are sorry that the description of the determination of ν_i on p. 24828 might not be clear enough. This is going to be improved in the revision. Our reply to S. Kreidenweis, item 6 p. 3,4, which is a revised description of the solution method, addresses your comment.

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Of course, we could think of putting the equations of A and B into (16b), and RHD being known, solve it for ν_i by some numerical recipe. Then, ν_i being considered almost constant (line 14, p. 24814), we could use (16a) . . . But this looks not practical to me: we do not know if the numeric al method will always converge and if it does, how long it will take and if the solution is unique.

ν_i is determined with Eq. (16b), i.e. Eq. 16a(RH=RHD, $\mu_s = \mu_{s,sat}$). Subsequently ν_i remains constant, when Eq. (16b) is applied. We thank you for the hint that we haven't discussed the solution of Eq. (16b). This will be revised and the following figures will be appended, which clearly show that for all choices of A,B and K_e (see Eq.(17a-d)) Eq. (16b) is good-natured and has a unique solution in ν_i , which is easy to find with any simple root-finding algorithm. e.g. bisection method. Since ν_i remains constant, this can be done during model setup and ν_i can be stored as lookup-table.

A deeper look could yield the following conclusions:

- 1. A and B are functions of ν_i and μ_s only, saturation or no.*
- 2. (16a) is an expression between three variables : RH, μ_s and ν_i , with the 2 (unexplained) expressions A and B (computed for saturation or not),*
- 3. (16b) is (16a) computed for saturation only, and leaving (RH= RHD known, $\mu_s = \mu_{s,sat}$ known) only one variable ν_i , with A and B,*
- 4. replacing A and B into (16b) makes it an expression with only one variable, ν_i , but valid for saturation only,*
- 5. so the value of ν_i , on is calculating with (16b) is for saturation only,*
- 6. therefore, if you want to use it elsewhere, it is essential to claim that $\nu_i = \text{constant}$ for the whole domain.*

Indeed, we assume that $\nu_i = \text{constant}$, as stated for example in the abstract or on p24824, line 21-22. A and B are explained in Sect. 3, p24827, line 12-21. The choice for the terms K_e , A and B in Eq. (16a) depends on the RH-range that should be covered by EQSAM4:

1. $RHD < RH < 95\%$: $K_e = 1, A=1, B=0$, i.e. μ_s Eq. (17c)
2. $RHD < RH < 98\%$: $K_e = 1, A=1, B_{98}$ Eq. (20), i.e. μ_s Eq. (17d)
3. $RHD < RH < 99.9\%$: $K_e = 1, A$ Eq. (18), B Eq. (19), i.e. μ_s Eq. (17a)
4. $RHD < RH < RH_{Scrit}\%$: K_e Eq. (1), A Eq. (18), B Eq. (19), i.e. μ_s Eq. (17b)

A, B and K_e only depend on the solute molality once ν_i is determined. We note that saturation is only required when determining ν_i with Eq. (16b), while Eqs. (17a-d) are not restricted to saturation. This will be stated more clearly in the revised manuscript.

I'm afraid you cannot do otherwise than use an equation like (16b), because you need measurements at saturation where $RH = RHD$ and $\mu_s = \mu_{s,sat}$ are both known.

We do not share this concern. Instead we see it as a clear advantage of the ν_i method that we only need two measurement values (and really only these two), i.e. the RHD and the mass fraction solubility w_s (or $\mu_{s,sat}$), to determine ν_i (with Eq.16b and the application dependend choice for A,B and K_e) and then we are able to solve Eqs. (17a-d) for the entire range of water activity ($a_w = 0 - 1$).

The further development is based on a lot (too much ?) of assumptions and simplifications for the results to have any practical use:

1. *A, B are functions of ν_i and saturated molalities only (p. 24827)*

A and B vary with molality, since Eqs. (18) and (19) are a function of molality μ_s and are not restricted to the saturation molality, $\mu_{s,sat}$. However, we can apply (18) and (19) at saturation together with (16b) to solve for ν_i .

2. *ν_i is constant (line 14, p. 24814),*

This is the core advantage of the ν_i method.

3. *considering two kinds of single solutes in binary solutions (line 1, p. 24817),*

The ν_i method is not restricted to two kinds of single solutes in binary solutions as demonstrated in the EQSAM4 companion paper.

4. *ideal solutions (line 7, p. 24814),*

The ν_i method is not restricted to ideal solutions.

5. *large relative humidity (line 7, p. 24814),*

The ν_i method is not restricted to large relative humidity, i.e. ideal solutions.

6. *volume additivity (line 1, p. 24819),*

Volume additivity is widely assumed (also for the κ method).

7. *$K_e = 1$ (line 16, p.24828); seems not necessary).*

K_e is required to consider different particles sizes with the ν_i method.

Our work is based on some useful assumptions, simplifications and empirical findings and the results are clearly of practical use. Even the simplest single parameter version of our model Eq. (17c) is applicable to sodium salts at high concentrations, which is not the case for the κ -method. Note that Eqs. (17a-d) are all single parameter models depending only on ν_i and describing a functional relation between RH and molality

μ_s . They are the rearranged Eq. (16a) with the A,B and K_e term specified according to the RH-range of model application. Furthermore, the ν_i -method is especially of use for mixed solutions, since Eq. (17d) can be solved analytically for various major compounds relevant to atmospheric aerosol modeling, as shown in the companion paper – published for discussion at GMDD: <http://www.geosci-model-dev-discuss.net/4/2791/2011/gmdd-4-2791-2011.html>.

This is another major advantage of ν_i compared to other methods.

In my opinion it is not necessarily good tactics to delay confidence in a paper until the disclosure of results in "companion papers" :

1. *Explicit derivation (lines 13 to 15, p. 24827),*
2. *EQSAM4 (lines 22 to 23, p. 24814, and line 11, p.24817),*
3. *Box model inter-comparison (lines 22 to 25, 24817)*

There is no need for a disclosure of results in "companion papers". The results presented deserve publication on their own merits for the reasons mentioned above and those mentioned by the referees. We mentioned the companion papers as they may be of interest for other readers. We will correct the cross-referencing in the revised manuscript.

Specific comments:

1. *(line 6, p. 24814) : The "(1) wide applicability" has not been shown in this paper. We do not agree. Our results are applicable to the whole range of water activity observed in the atmosphere, which is a wide applicability. This will be made clearer in the revision.*

2. *(line 6, p. 24814) : The "(2) simplicity" is only true if the assumptions hold and if one knows beforehand the values of the different ν_i .*

The assumptions hold, i.e. ν_i can be pre-determined. This is the beauty of the ν_i -method. ν_i can be easily obtained from two single measurement values with the equations presented, and then applied. And simplicity is justified since our assumptions hold for the two compounds discussed in this work, but also for various other compounds, which are of interest for atmospheric modeling and applied in the EQSAM4 companion paper.

3. *(line 6, p. 24814) : What does "(3) analytical nature" mean here ?*

Analytical nature means that the ν_i -method does not require an iterative determination of the required parameter to calculate the water activity, as it is the case for e.g. activity coefficients, which change as the water activity change.

4. *(lines 14 and 15, p. 24814) : What are these findings, where do they come from ?*

The findings, i.e. results, presented in this work, i.e. that ν_i can be held constant for the whole range of water activity. This will be clarified in the revision.

5. *(lines 24 and 25, p. 24817) : Wouldn't it be better not to make reference (p.24843) to a rejected paper ?*

The Xu et al., paper is not rejected. The status is that a revision is foreseen and in progress. This will be clarified in the revision.

6. *(lines 13 to 18, p. 24818) : In my opinion, the term "proportionality" is not correctly used here. The related explanations are not convincing.*

The term "proportionality" is used in accordance to the literature but will be changed to "dependence".

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7. (lines 13 to 15, p. 24824) : 1 mole of pure solute dissolving in 1 kg initially pure water is indeed 1 mol/kg but it is not an "initial concentration" of any kind : initial to what ? μ_s^o is just some additional constant with units.

μ_s^o is a constant with units 1 mol solute per kg water referred to μ_s^o as the initial concentration of the 1 mol solute that dissolves in 1 kg water considering stoichiometry. μ_s then refers to equilibrium of the mixed solution with the solute dissolved. However, we will refer μ_s^o as "reference molality" in our revised manuscript.

8. (lines 1 to 4, p. 24828) : Why "it should be possible" ? Is there a hidden limiting factor somewhere ?

The results show that it is possible. No hidden factors.

In my opinion, this paper needs a deep rewriting.

We will revise the manuscript according to the critical and constructive comments of the reviewers.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 24813, 2011.

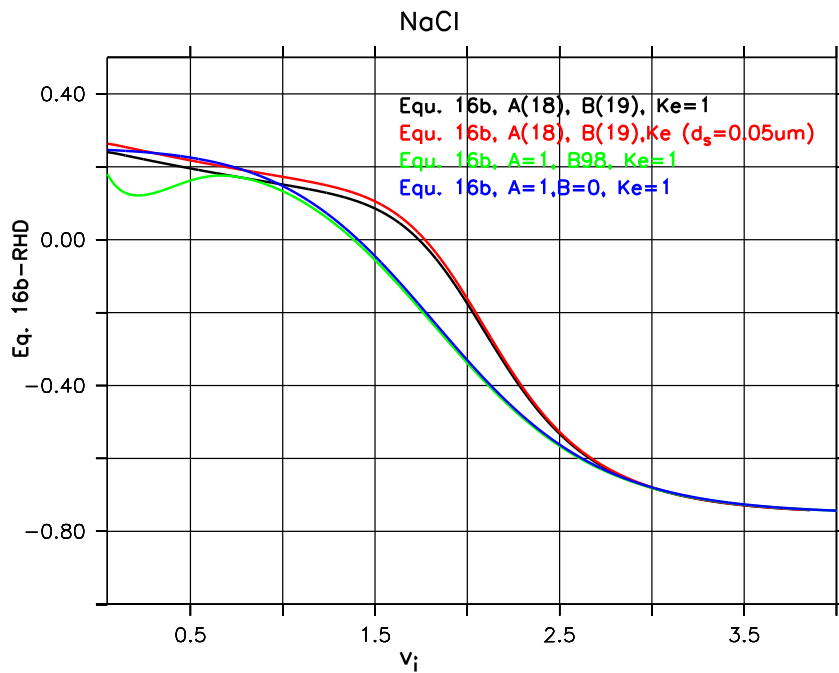
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Fig. 1.

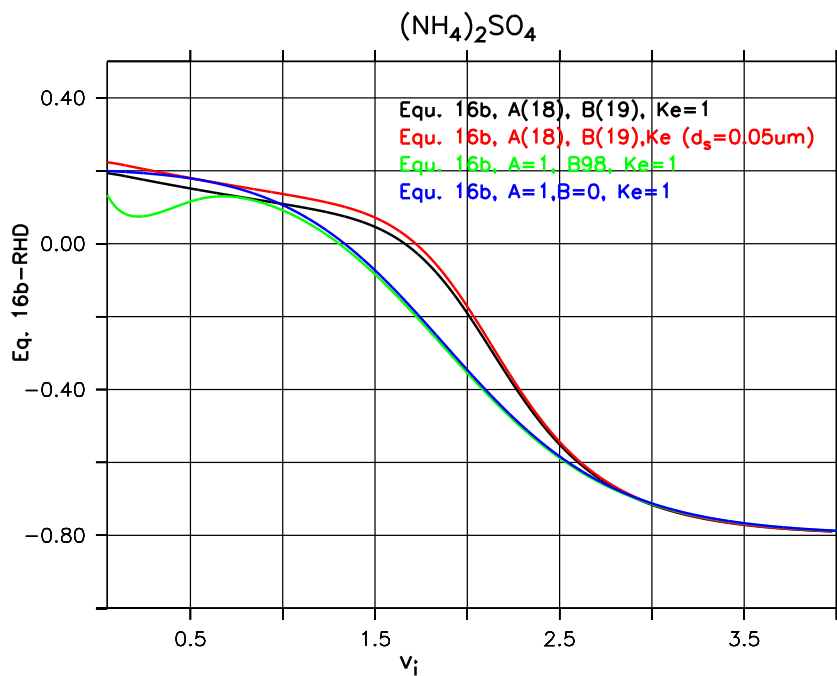
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Fig. 2.

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