

Interactive comment on “Partial Derivative Fitted Taylor Expansion: an efficient method for calculating gas/liquid equilibria in atmospheric aerosol particles – Part 2: Organic compounds” by D. Topping et al.

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Received and published: 3 November 2011

We thank the referee for the comments made which are addressed in the following.

‘As detailed in “specific comments,” I hesitate to recommend publication until thorough justifications for using (1) the Taylor Series expansion and (2) the chosen concentration scales are made for organic systems. There are also a large number of errors throughout the manuscript that require careful attention (addressed in “technical corrections”).

Specific comments: The work by Zaveri et al., 2005 (the MTEM model) is specific to

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aqueous inorganic electrolytes systems only. It is also specific to an ionic mole fraction concentration scale. The observation of linearity noted in the current manuscript (p1757, lines 10-13) was appropriately used by Topping et al., 2009 (the PD-FiTE model) for inorganic systems, but is inappropriately used here for organic systems. Before the PD-FiTE methodology is applied to organic systems (p1757, lines 23-25), proof of a linear dependence of the logarithm of the activity coefficient on some specific concentration scale is required.’

Response: Unfortunately it appears that the basis of this work has been misinterpreted, perhaps caused in part by our description, which we apologise for. This framework is not based on a collation of empirical observations (e.g. MTEM), nor founded on a detailed theoretical physical basis (eg UNIFAC), and we make no claim otherwise. In the abstract we state how this framework is based on the same ‘fitting methodology’ of the inorganic PDFiTE model rather than on its empirical basis. That is to say, as we applied in the inorganic PDFiTE paper, the polynomials used to represent different terms within a simple Taylor Series Expansion are ‘optimised’ using a more complex benchmark model (in this case the UNIFAC model). This lends itself to derive the model name: ‘Partial Derivative Fitted Taylor Series Expansion’. The general Taylor Series expansion provides a convenient basis for developing a reduced complexity representation of any multi-component system, whether or not it is possible to express terms within this expansion using an empirical basis. In this paper the main aim was to assess the performance of a framework based on said Taylor series expansion, by choosing concentration scales used within more complex models and optimising parameters in the fitting process. We have not used an ‘ionic’ mole fraction scale and do not feel it is inappropriate to base the framework on a Taylor Series Expansion. In the second paragraph we reference the development of the inorganic model, which we accept may cause confusion: ‘[inorganic PDFiTE] is based on the observation that the logarithm of activity coefficients varied linearly as a function of water activity when expressed in terms of equivalent mole fractions (Zaveri et al., 2005). Following this, Topping et al. (2009) developed a numerical expression based on ion-pairs and optimised interaction

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parameters using the thermodynamic model ADDEM (Topping et al., 2005). In the current manuscript we develop a similar reduced complexity expression for the activity coefficients of organic solutes.' Further down this page, on line 23 we then state : 'Following inorganic PDFiTE, in this paper we use the same Taylor Series expansion methodology to develop a model for organic solutes in aqueous solutions via an appropriate representation of multi-component concentrations and interactions.' Following the above discussion we suggest replacing this sentence with the following: 'Whilst the terms within the inorganic PDFiTE Taylor Series Expansion are based on empirical observations of activity coefficient variation, the development of the organic model in this paper is not. Rather, in this manuscript we test the applicability of another Taylor Series Expansion applied to organic solutes in water, where the model parameters are derived solely to ensure correct limiting behaviour and interaction terms derived by fitting this framework to a more complex benchmark model (UNIFAC). This fitting methodology is the same methodology applied to inorganic PDFiTE, despite the different approach used in defining the model terms and concentration scales, hence we use the same acronym here. ' This sentiment can then be re-iterated in section 2, and in the abstract, after the statement: 'In organic PD-FiTE, choice of concentration scale can be chosen according to the limiting requirements of the numerical framework'. Specifically, we can add the following line:' The numerical framework of organic PDFiTE is not based on empirical observations of activity coefficient variation, rather the same parameter fitting methodology is used as the inorganic framework,as detailed in section 3. The ability of this new framework to replicate activity coefficients for various concentrations is given in section 4 where the UNIFAC model is used as a benchmark.' Regarding this latter point, it was deemed very important to test this framework against systems of atmospheric importance using a benchmark model. This is why we chose the most abundant compounds in the condensed phase extracted from a recent sensitivity study that employed a commonly used gas phase degradation mechanism. With the development of re-tuned UNIFAC models and the emergence of the AIOMFAC model, it is unnecessary to compare directly with empirical data for multi-component systems

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where empirical data is likely to be scarce. It would be very interesting to perform a thorough comparison of available 'reduced complexity' formulations for activity coefficients against the current benchmark models (UNIFAC, AIOMFAC) to assess where the biggest sensitivities lie. For example, do the Wilson equations, which have a physical basis, perform better/worse than the PDFiTE equations and what level of accuracy is acceptable for simple metrics such as SOA mass? There are studies relating the effect of including or neglecting non-ideality within mechanistic models, but they rely largely on a subset of available benchmark methods.

'p1759, lines 9-11: It is stated that "[f]or the organic model, binary activity coefficients and interaction are expressed as a function of water mole fraction." The "two-fold" reasons for the change from water activity (RH) to water mole fraction are both reasons of convenience. A mathematical or physical reason to justify the change from water activity (RH) to water mole fraction is required.' Response: There is no reason that the organic model couldnt have retained the use of a water activity scale if the organic compounds were fixed in place, as described shortly. As the reviewer has already pointed out, we cannot simply rely on the same empirical observation used in inorganic PDFiTE. Thus, the choice of concentration scale was made with flexibility in mind, and the framework then tested against a benchmark model. The use of the water mole fraction does offer 'convenience', as the reviewer states, which in turn provides as with a mathematical flexibility to allow the compounds represented to change. Whilst we have used 13 compounds extracted from a recent sensitivity study to assess the model performance, these compounds are liable to change depending on the application of the model. For the inorganic model, the range of compounds defining the composition space was relatively small, and using the PDFiTE fitting methodology, the variation in water activity of the whole system was well constrained. In this instance, as new compounds are introduced, if the water activity scale were used, every model parameter would have to be refit. In this framework we treat interactions between binary pairs of solutes for a wide range of water concentrations, so as a new compound is re-introduced, only interaction terms between the new compound and existing com-

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pounds require fitting rather than every possible binary-pair. The other mathematical convenience is then the ability to use different models to calculate the water content, as the activity coefficient variations are expressed in terms of water mole fraction. Whilst the ZSR method is commonly used in aerosol modeling studies, there is no reason to suggest it will work well for all systems to be studied. This does have an empirical basis whereby the additive approach used in ZSR can exhibit deviations from laboratory studies of water uptake.. Similarly, there are coupled approaches developed to calculate water contents of mixed organic/inorganic systems.

'p.1760, line 17: It is stated that "[a]s the dry mole fraction of solute "B" approaches zero, the term . . . converges to zero." How would the reader know that the change of the log of the activity coefficient with respect to the concentration of the other species tends to zero as the concentration of the other species tends to zero? Justification is required here.' Response: In the document we state in the sentence before this that we are referring to the 'change' in activity coefficient of a compound 'A' due to another compound 'B' tending towards zero as compound 'B' vanishes. This is simply describing the fact that as compound 'B' vanishes in a ternary solution, the activity coefficient of 'A' converges toward its value it would have in a binary solution with itself and water.

Technical corrections:

'p 1756, line 15. "up to" not "upto".' Apologies, this has been corrected.

'Equation 2: The upper bound of the summation, 'N', has not be defined in the text. A sentence should be added to the text defining 'N' as the number of distinct compounds.' Response: This sentence has now been added: 'Where N represents the total number of solutes'

'p1758, line 5: The functional dependency on "(RH)" should be included (c.f. line 6 on the same page). Also, here and on p1760, line 14, "ln" should not be italicized.' Response: This has been corrected

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'p1758, line 7: "x_j" should be "x_i", or "component i" should be "component j".' Response: This has been corrected

'Equation 3: Subscript "i" should not be used both to define the species (LHS) and to index the summation (RHS).' Response: The equation has been corrected with the summation for 'i' removed and the term 'c_i' moved to the left of the summation for j.

'Equation 4 & 5: Again, the upper bound of the summation, m, is not defined. Please correct.' Response: The following sentence has now been added: 'where m represents the total number of compounds.'

'Equations 6-9: It is not clear why the concentration notation changed from "equivalent mole fraction" (x_w) in equation 1 to "associated mole fraction", (x) in equations 6-9.' Response: This seems to draw from the confusion discussed above. To aid clarification, the following sentence has been added after equation 6: 'As mentioned previously, organic PDFiTE does not have the empirical basis used in constructing inorganic PDFiTE. In equation 2, the expression x" refers to equivalent mole fractions. In the first instance, the Taylor Series expression used for organic PDFiTE is expressed using mole fractions of components in the multicomponent mixture (including water).'

Equation 6: The dependency on RH should be made explicit (similar to the way the x_w dependency is given in equation 7).' Response: In the discussion following this equation we propose using the mole fraction of water rather than RH. Given the second criticism the reviewer has made, expressing the dependency on RH explicitly here might be confusing. Therefore, we propose adding the following text to clarify this issue directly after equation 6: 'As inorganic PDFiTE was based on the empirical observation that the logarithm of solute activity coefficients varies roughly linearly with water activity, thus RH for a bulk solution, equation 6 would be written explicitly as a function of RH were we able to use the same basis. As mentioned previously, this framework does not use the same empirical basis. For the inorganic model, the range of compounds defining the composition space was relatively small and, using the PDFiTE

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fitting methodology, the variation in water activity of the whole system was well constrained. For the organic model, it is likely that the compounds selection will change depending on the application, thus systems studied. Whilst the water activity scale could be used, given the fitting methodology 'optimizes' interaction terms, as new compounds are introduced every model parameter would have to be refit. To mitigate this problem, a different concentration scale is chosen. . . .'

'p1759, line 22: "water as the solvent becomes" should be "water as the solvent, Eq. (6) becomes".' Response: This has been corrected

Equation 9: The sum is over index 'j', however, there are no subscripts 'j'. The summation is not needed.' Response: This has been corrected

'p1760, line 4: "With" not "With".' Response: This has been corrected.

p1760, line 14: The partial derivative should be taken with respect to "xB" or "x'B", not "B". Response: This has been corrected.

p1760, line 21: The constant of differentiation should read "xw = c" not "xw". The LHS of eq. (14) and should not be in parentheses. Response: This has been corrected.

Equation (15): The polynomial order superscript should be on the dry mole fraction, not on the subscript. Response: This has been corrected.

p1762, line 2: $\ln A(x'B, \dots, xw)$ should read " $\ln A(x'B, xw)$ ". Response: This has been corrected.

p1762, line 11: the arguments of beta should not be subscripted. Response: This has been corrected.

p1763, line 24-25. The original ZSR paper is Zdanovskii's 1936 paper, not Zdanovskii's 1948 paper. Please correct the citation. Response: This has been corrected.

Equation (17): The argument of the mole fraction of water should not be subscripted. Response: This has been corrected.

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p1764, line 12. In this line, eq. (B1) is referenced, but this is the same as eq. (13). At this point in the manuscript, it makes more sense to refer the reader back to an earlier equation, rather than forward to the appendix. Response: This has been changed to refer back to equation 13.

p1771, line 3: "Focused", not "Focus". Response: This has been corrected.

p1773, line 16: "Cloud", not "CLoud" (the "L" in VOCALS comes from the word "Land"). Response: Apologies, this has been corrected.

Figure 1: The caption and text say "x'B" (dry mole fraction of B), but the x-axis uses "XB" (the mole fraction of B). Please be consistent. Response: The figure axis has been changed.

Figures 2-3: Although it is explained in the text, it is confusing to use 1, 3, and 4 in the captions and A and B in the figures. A note similar to that seen with Tables 6-7 would be helpful. Response: A reference to the compounds listed in tables 6-7 has been added to the figure caption.

Figure 4: The caption refers to subscripts "b" and "t", but "b" and "t" are not actually subscripted in the figure. Please correct. Response: Apologies, these subscript references have been removed.

Figure 6: "RH)" instead of "(RH)". Response: This has been corrected.

Interactive comment on Geosci. Model Dev. Discuss., 4, 1755, 2011.

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