

# Interactive comment on “Treatment of non-ideality in the multiphase model SPACCIM – Part 1: Model development” by A. J. Rusumdar et al.

**Anonymous Referee #1**

Received and published: 9 July 2015

Review of Rusumdar et al:

The paper presents a new approach to couple a generic group contribution activity coefficient model within the dynamic SPACCIM model. I fully support the author's scientific rationale for including non-ideality in general dynamic models. All too often the influence of non-ideality is ignored through considerations of computational expense at the danger of biasing sensitivity to other processes/composition dependent effects. I do however have a range of general and minor comments I believe the authors should respond to before consideration for publication. The work is clearly substantial, but the presentation of the new work is not clear to suggest the paper has the correct balance of material, which no doubt already exists. The minor comments generally revolve around typically vague statements, or professions of model improvements without appropriate contextualization.

The authors would like to thank the Anonymus Reviewer#1 for the careful consideration of the manuscript and for the constructive comments and suggestions made to improve the manuscript. According to the reviewer's comments, the authors have further improved the manuscript. All comments and changes in the manuscript are addressed below. In the case, we do not concur with the reviewer's comments, adequate reasons are given. Finally, it is noted that the manuscript was again carefully checked for language and writing inaccuracies.

## **General comments:**

My general comments stem from section 2.3 and the apparent view from the abstract and introduction, that a new activity coefficient model has been developed to warrant the new reference ‘SpactMod’. If the basis from AIOMFAC has indeed changed, this should be clearer in the document. However, on inspection of the presented equations, it seems to be the same theoretical framework as presented by Zuend et al (2008) in which case the model appears to be AOMFAC with new interaction parameters. Is this because you have not performed a full parameter refitting across all interaction terms that you have decided to re-brand the model? Section 2.3.1 covers the theoretical background behind activity models derived from the derivative of the Gibbs excess energy. I read this section with the assumption of an adjusted theoretical basis following a similar derivation. I appreciate the presentation of the background, but this section could be much shorter with reference to Zuend et al (2011) and (2008) and where the new parameters fit in the model, without the Gibbs excess terms. I note you have worked with the AIOMFAC developers in the acknowledgement but still find the presentation of already available derivations and lack of information regarding parameter refitting a pity. As I said in the introduction, I believe the work is useful and the presentation of the novelty of this work be reformulated.

## **Author's response:**

The authors would like to clarify several ambiguous formulations and misunderstandings. First, the overall goal of the present work was not the development of a new activity coefficient model. The present paper aimed at the implementation of solution non-ideality in aqueous-phase reaction kinetics in the SPACCIM framework. Therefore, we have incorporated only a “new” activity module in SPACCIM to take into account non-ideality in the multiphase chemistry, especially, for small droplets and deliquesced particles. The extensions of the kinetic framework of SPACCIM are described in Sect. 2. A main goal of the

extended approach (Fig. 2) is to provide appropriate activity coefficients for solved species. Therefore, several activity models have been tested and compared regarding their suitable applicability in order to achieve the above-mentioned objective. Several results of the comparison are presented in Subsect. 3.1 and 3.2. Overall, AIOMFAC seems to be most qualified for the aimed applications. Hence, the theoretical framework and the available parameters of AIOMFAC have been applied for the implementation of the related module in SPACCIM. However, the present study also tried to include additional parameters without any parameter fitting. The approach of mod. LIFAC can be rewritten in the AIOMFAC formalism (see Appendix A). So, we can additionally use the related parameters of this approach to consider further possible interactions not included in AIOMFAC (Zuend et al., 2008). All modifications and additional parameter of SpactMod with respect to AIOMFAC are highlighted now in the revised manuscript.

The authors agree to some point that the main concern and the role of the implemented activity module SpacMod are pointed out not adequately enough in the manuscript. In the revised version, we clarify this in several places. Furthermore the authors agree that the presentation of the used AIOMFAC framework in Sect. 3 is very detailed. However for readability and clarification of the modification, the authors consider a description of the applied AIOMFAC framework close to Zuend et al. (2008) to be necessary.

The referee is right that new parameter refitting was not performed. However, the present work was aimed at building a kinetic model framework that can access the solution non-ideality at the core based on the available interaction parameters. This paper highlights the selection and implementation of a robust activity coefficient model approach that can predict the activity coefficients in relative humidity range important for ambient deliquesced particles.

Page 4174, line20. ‘based mainly on AIOMFAC’. What do you mean by ‘mainly’. This forms the crux of this section. By ‘mainly’ it seems you are referring to a reliance on the core of previously published interaction parameters rather than an extension of the theoretical basis. Is this correct?

**Author's response:**

With the word “mainly” the authors refer to the model derivation and the fitted interaction parameters that were given in Zuend et al. (2008) as they were the basis for the presented SpactMod implementation. The text has been revised.

Page 4180, line 26. ‘it was found that [the] model produce[d] relatively better results in most cases in comparison with the parameters from standard UNFIAC only’. There are many aspects to this sentence. First, what statistics back this up? Does this cover a wide range of conditions and functionality? Where is the evidence? In addition, given that standard [parameters] in UNIFAC has been superseded by values fit to more recent and more comprehensive data sets, why is this surprising? It isn’t clear based on the discussion, that needs re-writing. This falls into the same concern I have regarding presenting an activity coefficient model development in a sparsely populated scientific evaluation given the introduction of a ‘new’ model. On the whole, I would have thought it much better to present a more thorough assessment of how the new interaction parameters were fitted, whilst accounting for, as best as possible, mitigation of both under and over-fitting. Indeed, I was expecting more figures showing the prescribed impact of the newly fitted parameters in simple mixtures and yet found only systems that can already be accounted for?

**Author's response:**

The statement relates to the comparison studies in Subsect. 3.2 (see Figs. 5-8). As mentioned before, we have not performed any parameter fitting (see response above). Due to the reviewers comment we have rephrased the manuscript text. Furthermore, we have added results of two new simulations (Figs. 8 and 9, new numbering) which emphasize the differences and identicalness between AIOMFAC, mod. LIFAC and SpactMod.

**Minor comments:**

Page 4156, line 7: 'newly considered non-ideality properties' is confusing. I presume you are referring to a study including non-ideality in the cloud model that has not been considered before. Please revise this sentence. I would suggest something like : 'The present study was aimed at presenting further development of the SPACIM model through treatment of solution non-ideality, which has never been considered before.'

**Author's response:**

As suggested by the reviewer, the text has been changed. The text now reads: "The present study was aimed at presenting further development of the SPACIM model through treatment of solution non-ideality, which has never been considered before".

Page 4156 line 20: This minor comment feeds into my general concerns in the general comments to follow. The note that AIOMFAC was selected as a 'base' model and extended by additional interaction parameters is clear. If the theoretical basis of said model, in any way has been similar altered, it must be stated here since it would justify the use of a bespoke name for such a framework.

**Author's response:**

Due to the reviewer comment, the sentence has been revised as follows:

"Based on an inter-comparison of different activity coefficient models and the comparison with experimental data, AIOMFAC was selected and extended by adding additional interaction parameters from literature for mixed organic-inorganic systems."

Furthermore, it is noted that, the differences between the AIOMFAC and the SpactMod implementation are more clearly highlighted now in the revised manuscript and the appendices at several places.

Page 4156: '...the performance and the capability of the applied activity coefficient module were evaluated by...and results of other thermodynamic equilibrium models'. Please be clear here what exactly you mean by 'thermodynamic equilibrium models'. Models such as GFEMN, E-AIM, ADDEM, MOSAIC, whilst covering various scales of complexity, represent thermodynamic equilibrium models in that they search for the equilibrium end point. They rely on activity coefficient models, which technically should not be covered under the same model description

**Author's response:**

In this context, the authors mean the comparison with other activity coefficient models. Thus, the sentence has been changed. "other thermodynamic equilibrium models" have been replaced by "other activity coefficient models".

Page 4157, line 2: I agree activity coefficients should be mandatory but within the context of trying to determine, through process sensitivity studies, the uncertainty through their neglect is 'low enough' to be justified.

**Author's response:**

The reviewer is right that current activity coefficient models introduce still large uncertainties and the effects of the solution non-ideality must be justified by experimental studies rather than model studies. The stated conclusion is therefore too general and definite. Thus, the sentence was slightly modified to degrade the statement.

Page 4157, line 3: 'Modeled activity coefficients implicate that turnovers of chemical processes...'. What exactly do you mean by 'turnover'? The reader will presume this is somehow related to a time related constraint?

**Author's response:**

Here the word "turnovers" implicates the mass fluxes of the chemical processes. This is not a time related constraint.

To clarify that, the manuscript text has been revised. The revised text reads: "chemical reaction fluxes".

Page 4157, lines 5 -7. Similarly, please clarify what you mean by ‘chemical ion processing’.

**Author's response:**

The authors mean that the “chemical processing of ions”. Each reaction considered in the multiphase mechanism is treated as individual process. Apart from the dissociations, by which ions are formed, each ion reacts with other compounds (either organic or inorganic). Hence, the combination of all the reactions in which the particular ion participates (by formation or degradation) gives the information of chemical processing of ions in the particles.

Page 4157, line 8: ‘...organic compounds are partly  $> 1$ .’ This kind of statement appears in a number of places throughout the document. Partly? Do you mean that a certain % of activity coefficients are greater than unity? For what conditions? Can you please clarify this.

**Author's response:**

Results indicate that some activity coefficients of the organic compounds considered in the multiphase mechanism were obtained  $>1$  e.g. for alcohols, some of the di-aldehydes and for the dicarboxylic acids (except dissociated organic ions). The detailed analysis will be presented in companion paper. In the manuscript, the sentence in the abstract has been replaced by “...organic compounds are in some cases larger than 1 under deliquesced particle conditions” in order to avoid confusions. Moreover, the sentence in the Summary chapter has been revised.

Page 4158, line 18. Please introduce the relevant scale of activity coefficients at the very beginning [mole fraction or molality].

**Author's response:**

Throughout the simulations including the sensitivity studies, activity coefficients are estimated on molality basis (please see, e.g., section 2.3.5 in the manuscript). To make this clearer at this point, we have added the basis already in the introduction.

Page 4158, line 26 ‘...ideal solution in aerosol models has to be abandoned and non ideal behavior has to be considered.’ Again, I generally support your strong view on this issue. However, it should really be contextualized. You do refer to previous studies that suggest neglect of certain inorganic-organic interactions can lead to lower errors than an attempt at their inclusion. I would suggest adding the caveat that a range of sensitivity studies, from models that can account for composition dependent processes, need to be carried out to support either inclusion or neglect.

**Author's response:**

The sentence “Hence, the assumption of ideal solution in aerosol models has to be abandoned and non-ideal behavior has to be considered.” was changed into “Hence, a recent review by Herrmann et al. (2015) suggested that for modeling of multiphase chemical processes in a concentrated solution, it is reasonable to consider the non-ideal behavior instead of assuming ideal solutions.” Furthermore, a remark has been added to the manuscript regarding the need of a range of further sensitivity studies with models accounting for composition dependent processes to clarify the role of the non-ideal behavior and, overall, its inclusion or neglect in aerosol chemistry models.

Page 4159, line8: ‘...effort has been devoted formerly to..’. Suggest removing formerly.

**Author's response:**

We agree to the reviewers comment and have removed “formerly”.

Page 4159, line 16: The comment on various numerical techniques based on energy minimization and their cost is slightly confusing. The cost of such schemes tends to derive not from the numerical core of that search, but from the cost of the activity coefficient model and the number of compounds used in calculations. Suggest adding more recent references here.

**Author's response:**

We approve that the number of compounds considered mainly governs the numerical costs. However, the applied numerical algorithm affects primarily the computational amount, especially, if we have in mind 3D applications where the equations have to solve in each grid cell. Nevertheless, the numerical expenses are somehow comparable for both approaches. The corresponding paragraph has been revised. The remark regarding the numerical efficiency is removed.

Page 4159, line 22. 'Only very few models exist that treat partitioning to an efficient and accurate thermodynamics model'. Again, what do you mean by efficient thermodynamics model? Is SPACCIM particularly efficient? I would recommend, if this is the case, it is stated somewhere clearly. Also, MOSAIC and ADCHAM, for example, represent both extreme points in the modeling spectrum. MOSAIC was developed to face challenges associated with capturing thermodynamics in a regional model, whereas ADCHAM by appearance tried to include every process into a chamber based box model in one study.

**Author's response:**

The whole paragraph has been revised and the phrase "an efficient and accurate" is not included in the revised manuscript. Accurate and efficient thermodynamic module means that apart from the estimation of activity coefficients, the thermodynamic module should reliably predict water content and vapor-liquid phase equilibrium in multicomponent aerosols at a given relative humidity and temperature. We claim that SPACCIM can estimate the above mentioned. Nevertheless, MOSAIC and ADCHAM are surely also accurate and efficient models.

Page 4159, line 25 onwards. Here the authors claim that interactions between organic compounds and inorganic components have remained elusive. This was true for some-time, but has improved significantly. The discussion on the range of organic compounds treated in up-to date activity coefficient models, specifically AIOMFAC, should be included here to put the argument into context. You have already included Zuend et al (2011) in the reference list, please include this in your discussion. It might be covered elsewhere so please make sure the text flows better in a new version. Indeed, I would consider grouping distinct discussions into the same part of the text: Existing activity models, current state of interaction matrices, why this study builds on these.

**Author's response:**

The authors agree and have largely revised the whole paragraph in the manuscript.

Page 4160, line 4 'is an object of intense research all along the last years'. Suggest 'has been the focus of many detailed studies'.

**Author's response:**

The authors agree with reviewer's comment and have modified the manuscript according to the reviewer suggestion. The revised text reads: "as well as detailed thermodynamic comprehensions of its non-ideal behavior, has been focus of many detailed studies."

Page 4160, line 18: 'the kinetic description of non-ideality in SPACCIM is elaborated'. This another awkward sentence to read. I would suggest 'This paper is split into x sections. In section x, we described the inclusion of non-ideality into the SPACCIM model. . .etc'

**Author's response:**

Following the reviewers comment, we revised the manuscript text. The revised text reads: "This paper split into 4 sections. In section 2, we described the implementation of solution non-ideality into the SPACCIM model. In subsequent subsections, the coupling between microphysics and multiphase chemistry models as well as the necessary adjustments of numerical schemes is discussed. In Sect. 2.3, the activity coefficient module is introduced, that is specifically designed to treat multicomponent mixed organic-inorganic aerosol particles. Section 3 presents an evaluation of the currently implemented activity coefficient module in SPACCIM."

Page 4161, line 18. Here you comment on the ability to account for a ‘detailed’ description of processing of gases and particles prior to cloud formation, during and after its life-cycle. Does this account for the effect of condensing components on the effected size distribution, thus microphysics, at the point of activation? Note there has been some papers discussing the impact of co-condensation on increased cloud droplet numbers.

**Author's response:**

In the manuscript it was clarified that: “The droplet activation depending on the particle size and composition is explicitly described (see Sehili et al., 2005 and Wolke et al., 2005).” The SPACCIM microphysical model does consider the condensation of water and the chemistry model part takes into the account the corresponding uptake of water-soluble organic and inorganic vapors. Due to the close coupling (see also Sect. 2.2.4 and 2.2.5), a feedback, e.g., due to co-condensation is considered in SPACCIM (see also Author's response on the next comment).

Due to the reviewer comment the text in Sect. 2.1 has been extended as follows:

“Changes of the chemical aerosol composition by gas scavenging and chemical reactions feed back on the microphysical processes (e.g., water condensation growth rates via changes in the Raoult term). Consequently, related processes such as co-condensation (see, e.g., Topping et al. (2013) for details) are considered in the model.”

Page 4161, line20: ‘An advanced coupling’. What is it ‘advanced’? Are the other developments ‘advanced’?

**Author's response:**

“Advanced” means a (two-way) coupling between microphysics and multiphase chemistry in both directions). The feedback of chemical composition on explicit droplet activation (by Raoult term and surface tension) is considered. Furthermore, the coupling scheme is adjusted to the used implicit time integration scheme. However, as now discussed in Subsect. 2.2.6, only a simplified surface tension approach is used currently and should be advanced in future SPACCIM versions.

We replaced “advanced” to “robust and efficient” and changed the next sentence into “The coupling scheme is adjusted to the applied time integration method and provides ...”.

Page 4162, line 4: ‘The used chemical mechanism’ is awkward. I would suggest ‘the chemical mechanism used is provided as an input file’.

**Author's response:**

According to the reviewer comment, the text has been changed and now reads: “The applied multiphase chemical mechanism (including phase transfer data and kinetic reaction constants) is provided as an input file.”

Page 4163, line 7, ‘Mainly, the aqueous concentrations ...’ what do you mean by ‘mainly’? Is this a dominant feature somehow of the model development? Please clarify.

**Author's response:**

“Mainly” was changed to “In particular”.

Page 4164, line 13. Here you introduce the reliance on Henry’s law coefficients. Given the drive to include non-ideality in the model, how do you know, for a wide range of atmospheric compounds, that Henry’s law coefficients are more constrained than pure component vapour pressures? Do Henry’s law coefficients cover the same range of functionality that has driven you to extend activity coefficient model interaction parameters?

**Author's response:**

The SPACCIM model is designed to treat processes of aqueous aerosol particles and cloud droplets. Therefore, the phase partitioning of soluble gas phase compounds into the aqueous phase of deliquesced and cloud phase is described based on the Henry’s law. However, the Henry’s law constants of an aqueous solution depend on the composition of the aqueous solution. For example, they depend on the ionic strength (electrolyte identity) of the solution.



Non-ideal electrolyte solutions are able to both suppress the uptake below the value expected for pure water uptake (“salting-out”) and enhance uptake of the soluble gas (“salting-in”). The salting effects can be quantitatively described by the Setschenow equation (Sander et al. 2015). However, as reported in the review of Sander, there are unfortunately only some data available at current. Therefore, salt effects are only considered in the present SPACCIM model developments due to the consideration of the activity coefficients in the uptake calculation. Therefore, the reviewer is right in saying, that the Henry’s law coefficients do not cover the same range of functionality as activity coefficient models.

According to the reviewer comment, the authors have extended the model description part (Sect. 2.2) in order to address the issue and the current limitations due to salting effects.

Page 4166, section 2.2.3. I have a few issues when reading the section regarding terminology. You introduce a saturation vapour pressure, but relate this to the molality of the compound in question. I believe you should be referring to an equilibrium vapour pressure above the solution droplet? Saturation vapour pressure relates to the vapour pressure above a solution of the pure component [liquid or solid depending on the reference state]. Indeed, you then go on to refer to a ‘saturation vapour mole concentration.’ This does seem to be the case since you then express the [equilibrium] vapour pressure to the concentration in the gas phase at the same conditions.

**Author's response:**

Due to the author’s opinion, the terminology is correct.

Page 4168 line 25. ‘Eq1 is used to determine the equilibration of water between the liquid and vapour phase’. Does this mean you do not account for a dynamic condensation of water to the condensed phase?! If so, this could have significant implications for the prescribed micro-physics couldn’t it? Perhaps I have misunderstood this.

**Author's response:**

The water condensation is described dynamically and simultaneously for the whole particle/droplet spectrum. Eq. (1) describes only the equilibrium for a non-activated particle. This was pointed out at the end of Subsect. 2.2.5.: “Eq. (1) has to be fulfilled simultaneously for all non-activated particle classes. The droplet activation is described explicitly and takes place for all particles, which grow over the critical radius. The condensation and evaporation of the activated droplet classes are described dynamically. The predicted saturation vapor pressure is used as input into the droplet growth equation. The coupled system for all classes has to be solved simultaneously, whereas the total amount of water (liquid or gaseous) is prescribed.” However, we clarify here that Eq. (1) is only used “... for deliquescent particles.”

Page 4169, line 12. Please define precisely. Does mean other developments are not particularly precise?!

**Author's response:**

The author’s mean precisely is appropriate way. We have revised the sentence as follows: “On the other hand, the description of change in droplet curvature (Kelvin effect) is treated with surface tension approaches (see Subsect. 2.2.6).”

Page 4169, line 13: ‘Both effects are primarily appointed by the particle composition..’. Suggest replacing ‘primarily appointed’ by ‘influenced’.

**Author's response:**

As suggested by the reviewer, the text has been modified. “primarily appointed” was replaced by “influenced” in the revised manuscript.

Page 4170, section 2.2.6. I have many issues with this section, which will need a significant re-write. Please add a reference for the ‘almost’ linear approximation. What exactly do you mean by ‘almost’? Inclusion or neglect of surface tension has been the focus of many studies since the paper by Facchini et al (1999). I found it odd that there is not, at least, a brief

discussion as to why this particular equation was used. It is not enough to simply choose it based on convenience, as it isn't clear what effect it might have on your results. This particular formulation would lead to a significant decrease in surface tension at the point of activation. On the other hand, the studies of Sorjamaa et al 2004/Topping et al 2007/Prisle et al 2012 to name a few have since questioned the true meaning of surface tension, based on solving the Gibbs adsorption isotherm. The general study of Prisle et al 2012 indicated that using a range of models that can account for this effect can remove the previously held view of a significant impact from a decrease in surface tension but with appropriate caveats in the discussion. These studies need to be included in any discussion of any inclusion, or neglect, of a surface tension effect.

**Author's response:**

The "Surface Tension" subsection 2.2.6 was rewritten by considering the recommendations of the reviewer.

Page 4176, line 8 'are described same as original AIOMFAC', Suggest 'described as they are in..'

**Author's response:**

Following the reviewers comment, we changed the text in the manuscript to "The LR interactions described as they are in original AIOMFAC".

Page 4177, lines 17 – 19 really do not make sense. What exactly are you referring to with regards the statement: 'compensation of these inaccuracies is controlled by this simplification'. Please revise this.

**Author's response:**

The uncertainties occurred by using the properties of water (instead of using compound specific dielectric constants, densities), the semi-empirical MR part describes all the interaction effects involving ions not considered by the LR and SR contributions. This includes corrections to assumptions made in the LR and SR parts with respect to approximations of physical parameters.

Due to the reviewer comment, the text has been modified as follows:

The uncertainties occurred due to the adopted assumptions to derive the LR and SR activity coefficients with respect to approximations of physical parameters, were described in the semi-empirical SR part in the original AIOMFAC (Zuend et al., 2008)

Page 4180, line 22 'are also comprised in the SR part'. Replace comprised with 'included'.

**Author's response:**

As suggested by the reviewer, "comprised" has been replaced by "included".