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Interactive comment on “Improved AIOMFAC model parameterisation of the temperature dependence of activity coefficients for aqueous organic mixtures” by G. Ganbavale et al.

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The authors would like to thank Dr. Steven Compernelle (Referee #1) for his careful and detailed review of our manuscript and his valuable comments and suggestions. The suggestions provided and issues raised have helped us to improve this article. We address the Referee’s comments in our point-by-point response in the following. We will implement corresponding changes and clarifications in the revised version of the manuscript.

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General comments

Referee #1: This article will benefit from the following:

- A more detailed analysis on the improvement of AIOMFAC-P3 over AIOMFAC-P1 (see specific point 21 below).
- Evaluation to what extent some rather poor results of AIOMFAC-P3 are due to a bad starting point, i.e. AIOMFAC at room temperature, and a discussion what could be done to further improve the method (e.g. total refit, more functional groups, adaptations on the UNIFAC framework). See specific points 11 and 23 below.
- Reservations can be made about the data quality of SLE data for organic compounds (see also specific point 12). This is why [they] get a low w_d^{init} . Still, it could be that such data dominates the determination of specific parameters. This can be discussed. In Figure 1, apart from the number of data sets and the temperature range, also the median w_d^{init} (or another appropriate measure) can be specified as representative for the data quality.

Authors' response: We have improved the model comparison analysis between AIOMFAC-P3 and AIOMFAC-P1 as suggested under specific point 21 by this Referee. We discuss the first two points in the responses to the mentioned specific points below. Regarding the third point, we mention on page 16928 of the ACPD paper why SLE data of organic compounds obtained by application of Eq. (19) are considered less reliable than, e.g., water activity data from melting point measurements of aqueous solutions. Since we were aware of reliability issues with some of the SLE data obtained via thermodynamic conversions involving uncertain values of the melting point, enthalpy of fusion values etc., we looked carefully at these datasets and used

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comparisons with other data types, whenever possible, to ensure that the database and obtained interaction parameters are based on more than one type of data. There is not a single interaction pair whose parameters were determined based on SLE data only. However, where datasets are scarce, an SLE dataset may have a relatively large influence on the determined parameters. SLE data obtained with Eq. (19) were also, when possible, compared to the AIOMFAC model and other experimental data at room temperature, to judge whether a systematic offset exists at the reference temperature due to data conversion and uncertainties in physicochemical parameters involved in the conversions. We discuss details under specific point 12 below. We have considered the suggestion of the Referee and decided to include both the median and mean of corresponding w_d^{init} values in the database overview presented in Figure 1 (see the updated Figure 1 at the end of this document).

Manuscript revision: – Page 16986, Figure 1, the following changes are made:

Figure 1 and its caption are updated to include median and arithmetic mean of the w_d^{init} values involved in the database for the different main group interaction pairs.

– Page 16921, line 9: the following statements are added to the text:

In addition, listed are the median and arithmetic mean values of the assigned initial dataset weighting values (w_d^{init}) pertaining to each main group interaction pair. The combination of these values serves as an approximate measure of the data quality. A higher median value ($\text{median}(w_d^{init}) \geq \sim 1$), paired with a large number of datasets and a wide temperature range covered, indicates the availability of reliable thermodynamic equilibrium data for the model parameterisation. For certain group interactions, the data coverage and reliability is clearly lacking, which was considered in the model parameterisation.

Specific comments

1. **Referee #1:** Abstract, page 16908, line 25. 'overall improvement of 25%'. As C7803

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an abstract should stand on its own, you have to clarify here in what exactly the method has improved.

Authors' response: We clarify this sentence in the revised version and add additional information regarding the improvement at low and high temperatures, as detailed in the following. Also, the value of overall improvement was stated as 25 % but is actually more accurately 28 %, which is corrected in the manuscript.

Manuscript revision: – Abstract, line 22, the sentence is changed to:

The new AIOMFAC parameterisation for the temperature dependence of activity coefficients from low to high temperatures shows an overall improvement of 28 % in comparison to the previous model version, when both versions are compared to our database of experimentally determined activity coefficients and related thermodynamic data. When comparing the previous and new AIOMFAC model parameterisations to the subsets of experimental data with all temperatures below 274 K or all temperatures above 322 K (i.e., outside a 25 K margin of the reference temperature of 298 K), applying the new parameterisation leads to 37 % improvement in each of the two temperature ranges considered.

2. **Referee #1:** Page 16909, line 24. This is only true if thermodynamic equilibrium can be assumed for the aerosol. E.g. equilibrium calculations by themselves cannot predict the highly supersaturated aqueous salt aerosol above the efflorescence relative humidity. Please adapt the statement.

Authors' response: A supersaturated aqueous salt solution above the efflorescence relative humidity is by definition in a metastable state. If a metastable (instead of absolutely stable) equilibrium between gas phase and solution is assumed, thermodynamic phase equilibrium calculations (e.g. with AIOMFAC) can indeed be used to predict the water content and phase compositions in a system supersaturated with respect to inorganic salt content. The Referee refers here likely to the point that one needs to make a choice in a phase equilibrium

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calculation if supersaturated salt solutions should be allowed or not. This does not invalidate our statement, but we will add a clarification in the revised manuscript.

Manuscript revision: – Page 16909, line 23, the sentence is revised to:

Thermodynamic phase equilibrium calculations allow to determine whether the aerosol phase is a liquid (here liquid also refers to a homogeneous, yet potentially highly viscous amorphous phase), a crystalline solid, or a mixture of solid and liquid phases (when assumption of equilibrium is appropriate) and to what degree semivolatile species partition to the condensed phases (Pankow, 2003; Zuend et al., 2010; Zuend and Seinfeld, 2012; Shiraiwa et al., 2013). Furthermore, if the formation of crystalline phases is ignored intentionally in such calculations, metastable equilibria between the gas phase and supersaturated liquid solutions can be predicted.

3. **Referee #1:** Page 16911, line 25-26. State clearly if this is absolute or relative uncertainty.

Authors' response: We clarify that absolute uncertainty in water activity is meant here.

Manuscript revision: – Page 16911, line 25, the sentence is revised to:

The uncertainty in predicted homogeneous ice nucleation temperatures is stated as ± 0.025 in a_w (absolute uncertainties in a_w) in case of most of the data at higher temperature (at melting points) and ± 0.05 in a_w for all data collected at ice freezing temperatures (Koop et al., 2000; Koop, 2004).

4. **Referee #1:** Page 16911, bottom. The authors give here a good argument why increasing the low temperature range of an activity coefficient method is beneficial for atmospheric applications. But also the high temperature range of AIOMFAC is improved in this work. While this is probably less relevant for

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atmospheric applications, the authors could mention the benefit to the wider scientific community.

Authors' response: This is a good point, that we now include in a sentence at the end of the paragraph.

Manuscript revision: – Page 16912, line 3, the following sentence is added: In addition, the new AIOMFAC parameterisation introduced in this work leads also to substantial improvements in activity coefficient calculations at temperatures significantly higher than room temperature, which is of interest for applications in other fields of science and engineering, such as distillation.

5. **Referee #1:** Page 16911, bottom. “A small uncertainty in a_w of about 0.025 can change ... by 6 orders of magnitude”. Is the improvement of 25 % of AIOMFAC-P3 good enough to overcome this challenge?

Authors' response: This is a good question that is not easy to answer and the level of improvement differs clearly among aqueous organic mixtures of interest. Qualitatively, we think that the AIOMFAC-P3 parameterisation did make improvements in the direction of reducing the prediction error at the homogeneous freezing temperature of a number of aqueous organic solutions, however, for a large number of mixtures / datasets, the model prediction is still of higher uncertainty than 0.025 in absolute a_w value at those low temperatures. Further improvements of models, but more importantly of accurate laboratory experiments to train models like AIOMFAC/UNIFAC, are certainly highly desirable.

6. **Referee #1:** Page 16912, line 24. For clarity, state explicitly which AIOMFAC functionalities are not considered.

Authors' response: We add a statement clearly mentioning that inorganic ion groups are not considered and list the organic functional groups that have been introduced in the model previously in the context of the organic-ion interaction

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parameterisation of AIOMFAC (Zuend et al., 2011; Zuend and Seinfeld, 2012) that are not considered in this study. However, as stated on page 16912, the AIOMFAC model essentially includes a modified UNIFAC model that incorporates many more organic functional groups of less importance in atmospheric chemistry. Listing all of these groups as not being considered would not be helpful.

Manuscript revision: – Page 16912, line 24, the following sentence is added: Given the focus on organic + water systems, this work does not address the temperature dependence of interaction terms related to inorganic electrolyte/ionic components included in AIOMFAC. A few of the organic functional groups that have been considered explicitly in the AIOMFAC model development in the past are not included in this work. Those excluded organic functionalities are: hydroperoxide, peroxyacid, peroxide, peroxyacyl nitrate, and organonitrate, all introduced in the AIOMFAC model by Zuend and Seinfeld (2012) based on work by Compornolle et al. (2009). Note that these functional groups are available in AIOMFAC, but on the basis of the AIOMFAC-P1 model parameterisation only.

7. **Referee #1:** Page 16913, line 1-5. For completeness, state the appropriate temperature range of the inorganic part of AIOMFAC.

Authors' response: The appropriate temperature range for the inorganic part of AIOMFAC is the same as the one for the entire AIOMFAC model, which is stated on page 16912. The appropriate temperature range is “temperatures close to 298 K”. Here “close to” relates to, say, ± 10 K. However, more specifically, this value may vary from system to system since some aqueous electrolyte solutions show rather weak temperature dependence, so that a wider range around 298 K may often provide a good estimate of the activity coefficients. We add this point on page 16913.

Manuscript revision: – Page 16913, line 2, the following sentence is added:

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An estimate for the appropriate temperature range of AIOMFAC, when in addition to organic compounds and water also dissolved inorganic ions are included, is 298 ± 10 K. However, due to a rather weak temperature dependence of activity coefficients in aqueous electrolyte solutions, for many mixtures, the AIOMFAC model may also be applicable in a wider temperature range to good approximation (also relative to other uncertainties associated with a group-contribution model prediction).

8. **Referee #1:** Page 16914, line 9. Please clarify that these groups were introduced from Compernelle et al. (2009).

Authors' response: We mention the reference for the UNIFAC interaction parameters of these groups in the revised text.

Manuscript revision: – Page 16914, line 9, the sentence is revised to:

In addition, based on the approach and UNIFAC parameters determined by Compernelle et al. (2009), Zuend and Seinfeld (2012) introduced in AIOMFAC the functional groups hydroperoxide, peroxyacid, and peroxide, including estimated interaction parameters with the inorganic ions of the model.

9. **Referee #1:** Page 16919, top. To facilitate the discussion, an explicit equation relating the quantities of Eq (15) and (16) would be helpful.

Authors' response: The purpose of the comparison of Eqs. (15) and (16) is in explaining the chosen form of the temperature dependence expression for $\ln \Psi_{m,n}$. It justifies the expression of Eq. (16) based on thermodynamic reasoning for the form of an applicable temperature dependence, yet it leaves room for the set of parameters ($a_{m,n}$, $b_{m,n}$, $c_{m,n}$) essentially being fit parameters determined from experimental data. While being related, these parameters are not exactly 1:1 linked to the thermodynamic quantities (changes in gibbs energy, enthalpy, and heat capacity), as discussed on page 16918, lines 17 – page 16919, line 8.

We prefer to keep this comparison of the equations and related discussion in the given form.

10. **Referee #1:** Page 16919, line 1-8. To what extent can the parameters be separately used to calculate mixing enthalpies and mixing heat capacities of molecules? Or are they only appropriate taken together to calculate activity coefficients?

Authors' response: This is a good question that would require a more thorough investigation that goes beyond the scope of this work. Given the way the parameters were estimated and the form of Eq. (16), as discussed above, we advise to use the parameters only taken together for the purpose of calculating activity coefficients.

11. **Referee #1:** Page 16919, line 11-16. Backward compatibility is of course convenient, but should not be the only consideration. Could the AIOMFAC method not benefit from a refit of a_{mn} parameters, since some of them are quite old, and more data has become available since then? See also specific point 23 on the bad performance for aqueous 2-butoxyethanol.

Authors' response: We agree that there is potential in refitting certain $a_{m,n}$ parameters to aid in improving AIOMFAC predictions for certain aqueous systems, which we are also considering as an option for a small selection of group interactions, if sufficient experimental data is available. In this context, it is important to note that the $a_{m,n}$ parameter taken from the UNIFAC model parameterisation (from several revisions of that model parameterisation actually) have been determined based on a very large database (not all data publicly available) including many more functional groups than we are focusing on in this work. The refit of a subset of parameters therefore needs to be done with this in mind. A refit of the complete UNIFAC/AIOMFAC model is a huge undertaking.

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Presently, it seems highly advantageous to us, regarding more general applicability of AIOMFAC, to keep a high level of backward compatibility with UNIFAC. Nevertheless, the Referee is right that with the availability of new experimental data, a refit of a smaller subset of $a_{m,n}$ interaction parameters (potentially also of the ether group in 2-butoxyethanol) are of interest for future model development. We also discuss this aspect below in the manuscript revision under point 21.

12. **Referee #1:** Page 16922, Eq (19). Taking a constant $\Delta c_{p,m,i}$ at $T_{m,i}$ can lead to inaccurate or plainly wrong results if $T \ll T_{m,i}$. This approximation should be mentioned here. For example, in the case of malonic acid, the lower T data presented is about 130 K below the melting point of 406 K. Can the authors assess the accuracy of Eq (19) for such large temperature differences?

Authors' response: This is a good point and part of the reason why SLE data derived via Eq. (19) are generally considered by us to be of lower reliability than some other data types that do not involve a large temperature difference from the melting point to the data point. However, in our experience with these data, the issue is not so much in assuming a constant change in heat capacity at melting, as it is about the uncertainties related to the enthalpy changes and phase transition temperatures involved. If $\Delta h_{m,i}$, $\Delta c_{p,m,i}$, and, if applicable, the $\Delta h_{tr,i}$ values are known accurately alongside with accurate phase transition temperatures (including melting points at standard pressure), Eq. (19) does lead to quite accurate SLE activity data at lower temperatures. This is judged based on comparison to other data types of the same systems at the same low temperatures as well as to the AIOMFAC model predictions near room temperature for systems where the model performs well. Thus, we assume the problem is not with Eq. (19), but with sometimes quite uncertain values of the thermophysical data used with the equation. Based on comparisons of different datasets for the same system and with preliminary model fit runs, we identified

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SLE datasets where such issues were very likely the case and these datasets were excluded from the model fit.

Manuscript revision: – Page 16923, line 8, the following sentence is added:

We note that for certain organic compounds rather large uncertainties in the physicochemical property values used in Eq. (19) will translate into large uncertainties in the calculated SLE activity values, particularly when the target temperature is far from the melting point temperature at standard pressure. In this work, such uncertainties were assessed based on the comparison of derived activity values with activity values from other data types for the same system, and by means of preliminary model fits of AIOMFAC-P3. Affected datasets were either assigned a much lower weighting or zero weighting (removing the dataset from the fit).

13. **Referee #1:** Page 16923, line 12. Most of the water activity measurements presented here are within the range 289–307 K. If I understand well, they are therefore not considered for the AIOMFAC reparameterization. This should be mentioned.

Authors' response: This is correct: for the temperature range 298 ± 10 K, the measured water activity data were not used to fit the new AIOMFAC parameters. However data at higher/lower temperatures from water activity measurements were used in combination with other data covering a wide enough temperature range, discussed on page 16929. The purpose of performing a_w measurements close to room temperature as well, was to have a series of measurements at different temperatures for comparison and assessment against other data/methods.

Manuscript revision: – Page 16923, line 16, the sentence is revised to:

Measured water activities were then used directly for the AIOMFAC-P3 parameter determination – with the exception of data within ± 10 K from 298 K.

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14. **Referee #1:** Page 16924, line 11-21. The explanation provided here is unclear and seems to mix up two different approaches. The authors start with 'for the comparison of calculated relative activity deviations between the activities of components'. This seems to refer to the, computationally cheap, method of Zuend et al. (2011), (p 9166, second column), where calculated activities in two phases are compared. However then the authors continue: 'An initial mixture composition with mole fraction x_j^{init} ...' discussing a one-phase initial mixture composition. This seems to refer rather to the computationally expensive method (Zuend et al. (2011), p 9166, first column), involving the calculation of phase separation, and where calculated and experimental concentrations are compared.

Authors' response: The Referee is right. We revised these lines of text to clearly separate the two approaches used for (i) the fitting of LLE data based on the method of Zuend et al. (2011) and (ii) the comparison of LLE composition predictions from an initial mixture composition using the method of Zuend and Seinfeld (2013), which is used for graphical comparisons, but not for the fit of model parameters.

Manuscript revision: – Page 16924, line 6 – 24, the sentences were rearranged and revised to:

A direct calculation and comparison of activities in coexisting phases is possible at experimental LLE compositions, i.e., measured mole fractions x_j^α and x_j^β of the two liquid phases α and β at equilibrium. According to the reference state definitions of AIOMFAC, different independent components j should have the same activities in coexisting phases, i.e., $a_j^{(x),\alpha} = a_j^{(x),\beta}$. This data type can therefore be implemented in the model fit by minimizing the relative differences between the activities of the components in the two liquid phases. We use the method introduced by Zuend et al. (2011) for the comparison of calculated relative activity deviations between the activities of components j present in the two phases.

Furthermore, we also performed AIOMFAC-based predictions of the phase compositions at LLE using the method of Zuend and Seinfeld (2013), particularly

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for the graphical comparison of measured and predicted tie-line LLE data. To perform such predictions, an initial composition point is required from which a liquid-liquid equilibrium calculation is performed in order to determine whether the initial mixture composition is stable as a single homogeneous phase or whether two coexisting liquid phases represent the stable equilibrium state (according to the model) and what the compositions of the two phases are in the LLE case. An initial mixture composition with mole fraction x_j^{init} of component j on a unstable / metastable point of an experimental tie-line can be generated by: $x_j^{init} = \frac{1}{2} (x_j^\alpha + x_j^\beta)$. Such LLE predictions from an initial composition are computationally more expensive than the relative activity difference calculations used in the model fit, yet offer a different view on the performance of the model for applications of phase separation / phase composition computations.

15. **Referee #1:** Page 16924, line 22. What does 'forward computation' mean in this context?

Authors' response: This has been revised, see point 14.

16. **Referee #1:** Page 16925, line 26. What is the data source for fugacity corrections? What is the size of the 'moderate' fugacity correction for e.g. glycerol at room temperature?

Authors' response: We did comparisons of the experimental activity coefficients derived from VLE data for smaller alcohols with/without fugacity corrections. Fugacity correction terms (based on a virial equation of state, with second virial coefficients of a mixture) were applied following Marcolli and Peter (2005), with theory and data for the correction terms according to Tsonopoulos (1974) and Zemp and Francesconi, (1992). For glycerol, according to Oliveira et al. (2009), a rather complex "Cubic-Plus-Association (CPA) Equation of State" can be applied to obtain vapour pressure predictions over a mixture. As described

in the manuscript on page 16925, we did not apply fugacity corrections for the smaller alcohols. For glycerol, fugacity corrections would be required to make proper use of related VLE datasets, but were not applied in this work since a big effort would be required in implementing a rather complex CPA equation of state model just for such corrections. Instead, given the availability of enough datasets with alcohol functionalities in our database, the uncorrected glycerol VLE datasets were assigned very low weightings, essentially excluding their influence on the parameter fit. We add this information on fugacity corrections in the revised manuscript.

Manuscript revision: – Page 16926, line 3, the following sentence is added:

For glycerol, fugacity corrections were not applied; instead, given the large amount of datasets covering functional groups of alcohols, the glycerol VLE datasets were assigned a very small weighting, essentially excluding their influence on the parameter fit.

17. **Referee #1:** Page 16928, line 19-20. What about data sets with data partially in this temperature range? Are they not considered, fully kept, or is only the data outside the temperature range taken? If fully kept, is this not an issue regarding the goal of keeping AIOMFAC unchanged around room temperature?

Authors' response: There are only a few datasets with data points partially in this temperature range (289 – 307 K). These datasets were considered and fully kept. However, this is not an issue regarding keeping AIOMFAC unchanged around room temperature, since the influence of such data points is very small given that there is data for the main group interactions involved that goes far beyond this tight temperature range around 298 K. Furthermore, we describe on page 16929 that if for a specific main group interaction pair the temperature range covered by the database is limited to temperatures close to room temperature (i.e., covering less than 40 K in range), neither $b_{m,n}$ nor $c_{m,n}$ parameters

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were fitted. Thus, applying this procedure it is achieved that AIOMFAC is kept unchanged close to room temperature and that in cases where data is limited to close to 298 K, no potentially “wrong” temperature dependence would be introduced.

18. **Referee #1:** Page 16929, line 5-6. Define T_{low} , T_{high} .

Authors' response: We add the definition in the revised manuscript.

Manuscript revision: – Page 16929, line 4 - 6, the sentence is revised to:

These criteria are separately applied to each group interaction pair as follows: the $b_{m,n}$ values are determined only if: $\Delta T_{low} = |T_{low} - T_{\ominus}|$ or $\Delta T_{high} = |T_{high} - T_{\ominus}| > 40$ K and $\Delta T = |T_{low} - T_{high}| > 40$ K, where T_{low} and T_{high} are the lowest and highest temperatures covered by the data points involved (see Fig. 1) and $T_{\ominus} = 298.15$ K is the reference temperature.

19. **Referee #1:** Page 16929, line 16. Molar heat capacity and molar enthalpy have different unit types. You first have to specify their units before you can compare their numeric values. E.g. J/(mol K) for molar heat capacity and J/mol for molar enthalpy.

Authors' response: We assume SI units for both quantities and this is now clarified in the revised manuscript.

Manuscript revision: – Page 16929, line 14, the sentence is revised to:

These thermodynamic quantities tend to be of different magnitude. In the temperature range of interest here, molar heat capacity changes (units of $\text{J mol}^{-1} \text{K}^{-1}$) are roughly two to three orders of magnitude smaller in value than changes in molar enthalpy (units of J mol^{-1}).

20. **Referee #1:** Page 16929, line 20. On which basis have these particular limits

been chosen?

Authors' response: These limits are chosen based on characteristic values of the $a_{m,n}$ parameters and based on the reasoning discussed in the above point (and page 16929, lines 10 - 18) regarding the relative magnitude in changes of heat capacity versus enthalpy. Although, there is some arbitrariness in the expert judgement of what the exact bound values should be.

21. **Referee #1:** Page 16930, line 27. On F_{obj} :

- (a) Refer here to Eq. (22) where this quantity is defined. Also, restate explicitly that this only involves data sets not around room temperature.
- (b) The evaluation of the improvement should be more detailed. The sum in Eq. (22) can be split over data sets well below room temperature (giving rise to $F_{obj,low}$) and well above room temperature (giving rise to $F_{obj,high}$). For people interested in organic aerosol mixtures, especially the improvement in $F_{obj,low}$ will be of interest.
- (c) In the same spirit, F_{obj} should be split over $F_{obj,mono}$ and $F_{obj,poly}$, referring to data for monofunctional and for polyfunctional compounds respectively. Is there a significant improvement in $F_{obj,poly}$, which is probably of most relevance to aerosol mixtures?

Authors' response: We have considered these points and improved the evaluation of F_{obj} including subsets of the database, as suggested. The obtained values will be included together with an improved and substantially extended discussion of the comparison between AIOMFAC-P1 and AIOMFAC-P3 in the revised manuscript (see additions in the manuscript revisions below).

Manuscript revision: – Page 16930, line 22, the following statement is added: As discussed in Section 4.1, the database and therefore the values of F_{obj} (Eq. 22) evaluated with both AIOMFAC-P3 and AIOMFAC-P1 for comparison,

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do not include datasets with data points exclusively near room temperature (298 ± 10 K).

– Page 16930, line 23, the sentence is rephrased to:

In this section, we compare the model performance of the new AIOMFAC-P3 version with AIOMFAC-P1 (original AIOMFAC version) based on overall quantitative measures followed by a discussion of a selection of aqueous organic mixtures and water-free organic mixtures.

– Page 16930, line 25, the sentence is rephrased to:

The new AIOMFAC-P3 parameterisation for the temperature dependence of activity coefficients shows an overall improvement of 28 % in terms of F_{obj} in comparison to AIOMFAC-P1 (542 datasets involved).

– Page 16931, line 5, the following extended discussion is added:

For the purpose of evaluating the improvement of the new parameterisation it is of interest to compare the performance of the two AIOMFAC model versions for different subsets of the database covering separately low and high temperature ranges and certain aspects of the complexity of molecular structures involved (“monofunctional” vs. “multifunctional” organic components). We define the value $F_{obj,low-T}$ calculated as the objective function value based on Eq. (22) when exclusively considering datasets with $T_{high} < 274$ K. That is, the subset of the database including only datasets containing data points with a maximum temperature below 274 K (at least 25 K below the reference temperature of 298 K). This serves to represent the low-temperature range in our comparison. Analogously, to represent the high-temperature range (at least 25 K above 298 K), we define $F_{obj,high-T}$ by exclusively considering the datasets with $T_{low} > 322$ K. The minimum distance of 25 K from the reference temperature was chosen such that there is (i) a clear difference between the low and high temperature ranges considered, yet that (ii) still many datasets are included in the comparison (especially given that low-temperature SLE-derived water activity data often starts at the melting point temperature of pure water-ice).

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Based on this distinction into low and high temperature ranges and from the evaluation of $F_{obj,low-T}$ and $F_{obj,high-T}$ with both AIOMFAC versions, it is found that AIOMFAC-P3 improves similarly in both temperature ranges relative to AIOMFAC-P1. For the low-temperature range the improvement of AIOMFAC-P3 is 37 % (152 datasets involved; $F_{obj,low-T}(AIOMFAC - P3) = 10.207$), while for the high-temperature range the improvement is 37 % (223 datasets involved; $F_{obj,high-T}(AIOMFAC - P3) = 37.554$). The fact that the improvement is better in the lower and higher temperature ranges compared to the overall improvement (of 28 %) is not surprising. This is simply because the two additional fit parameters in AIOMFAC-P3 have a relatively small effect on the model performance in the ± 25 K range around the reference temperature. Therefore, the AIOMFAC-P3 improvement over AIOMFAC-P1 is expected to be better when the datasets covering the temperature range relatively close to room temperature are excluded from the model comparison (to clarify: these data are not excluded from the AIOMFAC-P3 fit – except for datasets within the 10 K margin around 298 K, which are also not considered in the overall model performance comparison). We further differentiate the low and high temperature subsets of the database each into two classes of (i) datasets containing monofunctional organic compounds only and (ii) datasets containing at least one multifunctional organic compound. The terminology applied here is to call an organic compound “monofunctional” when its molecular structure contains only one oxygen-bearing subgroup (e.g., phenol, 2-butanol, or palmitic acid), while glycerol, sucrose, 2-ethoxyethanol, glutaric acid, vanillylmandelic acid, and resorcinol are examples for multifunctional compounds included in our database (see Table 1). Despite this terminology, in AIOMFAC/UNIFAC the compounds termed monofunctional here are typically also composed of several types of subgroups (e.g., different CH_n and ACH_n groups in addition to an oxygen-bearing subgroup). Multifunctional oxygenated compounds are often found as major contributors to the total mass of the organic aerosol fraction (e.g., Hallquist et al., 2009).

The results from the evaluation with these subclasses in terms of average improvement of AIOMFAC-P3 compared to AIOMFAC-P1 for the low-temperature range are: 55% (46 datasets; $F_{obj,low-T,mono}(AIOMFAC - P3) = 5.197$) for the subset of datasets with monofunctional compounds and -7% (106 datasets; $F_{obj,low-T,multi}(AIOMFAC - P3) = 5.010$), i.e., a decline in agreement, in the case of datasets with multifunctional compounds. For the high-temperature range the average improvement is: 35% (162 datasets; $F_{obj,high-T,mono}(AIOMFAC - P3) = 31.237$) for monofunctional and 43% (61 datasets; $F_{obj,high-T,multi}(AIOMFAC - P3) = 6.317$) for the datasets involving multifunctional compounds. Note that these percentages reflect a weighted average improvement of AIOMFAC-P3 (weighting depends on the w_d^{init} values). There are some datasets for which the AIOMFAC-P3 parameterisation shows an improvement over AIOMFAC-P1 and in return there are some datasets for which the AIOMFAC-P1 parameterisation shows better agreement. In the case of the low-temperature range comparisons, for the subset of datasets containing monofunctional compounds, AIOMFAC-P3 leads to improvement in case of 34 datasets versus a decline in case of 12 datasets. For the low-temperature range subset of datasets containing multifunctional compounds, AIOMFAC-P3 leads to improvement in case of 50 datasets but decline in case of 56 datasets. Thus, while this evaluation shows that AIOMFAC-P3 leads to improvement with the experimental data considering the whole database, as well as for the subsets of low and high temperature ranges, the new parameterisation does also lead to a decline in agreement for a number of datasets with respect to the performance of the original AIOMFAC-P1 parameterisation. This is partly due to the nature of applying a global parameter optimization aiming at the simultaneous improvement of the weighted model-measurement deviations based on Eq. (22), which entails the possibility for reduced agreement for some systems as long as the overall model-measurement agreement increases. Moreover, the AIOMFAC-P1 parameterisation shows already good agreement with a part

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of the experimental datasets at low and high temperatures. For this fraction of datasets any changes in model prediction due to a new parameterisation may easily lead to a decline rather than an improved agreement with experimental data. However, as long as the changes in the model predictions are small for these systems, a decline in agreement relative to AIOMFAC-P1 could still mean that AIOMFAC-P3 performs well. Nevertheless, there are also datasets for which both AIOMFAC parameterisations show relatively large discrepancies (e.g., the water + 2-butoxyethanol system further discussed below). For such systems, additional improvements of the AIOMFAC model seem necessary – either by a new fit of certain $a_{m,n}$ interaction parameters (kept untouched in this work) or by introduction of additional (special) subgroups that help to account for the effects of certain intra- and inter-molecular subgroup–subgroup interactions (e.g., intramolecular hydrogen-bonding among oxygenated functional groups in close proximity). A thorough evaluation of these options and improvement of AIOMFAC in this direction is the topic of future work.

22. **Referee #1:** Page 16932, malonic acid + water example. Of all organic+water examples, this particular example is probably the most relevant for atmospheric aqueous aerosol. But in this case no significant improvement vs. AIOMFAC-P1 is present. Can the authors give another example -relevant for atmospheric aerosol- where the improvement of AIOMFAC-P3 can be demonstrated, or is this not available? See also point above on $F_{obj,poly}$: is there a significant improvement for polyfunctional compounds specifically?

Authors' response: For many dicarboxylic acid systems, the improvement of AIOMFAC-P3 with respect to AIOMFAC-P1 is small or absent in the lower temperature range. This is also shown by the malonic acid + water example. We chose this example because it also allows to show datasets for the higher as well as lower temperature range to be shown for the same binary system.

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For many other binary systems with multifunctional organic compounds, we do not have data in both temperature ranges that would be better examples. As discussed above (point 21), specifically regarding the datasets containing multifunctional compounds, improvement in the lower temperature range is only the case in about half of the systems, while for the other half of the systems AIOMFAC-P1 shows better agreement. There are systems with multifunctional compounds (e.g., sorbitol, 2,3-butanediol, resorcinol) for which AIOMFAC-P3 leads to noticeable, but not dramatic improvement at low temperatures.

23. **Referee #1:** Page 16933. 2-butoxyethanol + water example. This example shows no good agreement with both low T and high T data for AIOMFAC-P1 and AIOMFAC-P3. Could the reason be that the room temperature agreement of AIOMFAC is also bad, i.e. that the starting point is not good? This should be mentioned.

Authors' response: This is the case. For the 2-butoxyethanol + water example, the agreement between AIOMFAC and experimental data near the reference temperature of 298 K is not good. We will mention this in the revised text.

Manuscript revision: – Page 16933, line 29, the following statements are added:

The observed disagreement between both models and the experimental data is mainly due to the fact that there is already a clear discrepancy between AIOMFAC (both versions) and the experimental data near room temperature. Since there is already disagreement at the reference temperature (298.15 K), the new model parameters for improved temperature dependence ($b_{m,n}$ and $c_{m,n}$) cannot (and should not) remove this model–measurement discrepancy. This system illustrates that a re-parameterisation of certain $a_{m,n}$ group interaction parameters may be necessary to improve AIOMFAC for this and similar systems.

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24. **Referee #1:** This could be an argument that for significant further improvement, also the a_{mn} parameters should be reparametrised. Could the authors comment on this?

Authors' response: See the responses to points 11 and 23 above.

25. **Referee #1:** Table 1, caption. Mention that the data with $w_d^{init} = 0$ do not affect the reparameterization.

Authors' response: We add a clarification in the table caption.

Manuscript revision: – Table 1, caption, the caption text is rephrased to:

Table 1. Components, main groups, temperature range, number of data points (N_d), initial weighting (w_d^{init}) and references of “water + organic” and “organic + organic” datasets used (where $w_d^{init} > 0$) for the short-range parameterisation of organic main group ↔ water and organic ↔ organic main group interactions.

26. **Referee #1:** Figure 1, caption. Define here what 'substantially different' means.

Authors' response: The text of this figure caption has been amended to also include this information on the temperature difference, see the revised Figure 1 at the end of this document.

Technical corrections

1. **Referee #1:** Page 16910, line 19. “...(SLE) data, following the...”. Replace the komma by a point.

Authors' response: This is now corrected in the revised version.

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2. **Referee #1:** Page 16911, line 8. Remove “often”.
Authors’ response: Word removed.

3. **Referee #1:** Page 16922, Eq (19). In general there can be multiple transition points. So a sum over transition points would be more appropriate.
Authors’ response: This is true. We add a clarification in the related text.
Manuscript revision: – Page 16923, line 2, the following statement is added. Note that if more than one solid–solid phase transition is present in the temperature range of interest, additional terms (of the form of the second term) need to be added in Eq. (19) to account for each of these phase changes.

4. **Referee #1:** Page 16923, line 7-8. Put both references in one set of brackets.
Authors’ response: Done.

5. **Referee #1:** Page 16931, line 20-23. “Over all concentrations...” and “In comparison to...”. These two consecutive sentences say essentially the same thing. I would remove the first.
Authors’ response: The first sentence was removed.

6. **Referee #1:** Page 16932, line 11-12. "common functional groups". But this system (water+ acetic acid) does not contain compounds with common functional groups. Do the authors mean perhaps with "other systems" systems of type (water+ carboxylic acid)?
Authors’ response: Yes this is meant. We rephrased this sentence.
Manuscript revision: – Page 16932, line 11, the sentence is revised to:
This steeper slope of changes in water activity with temperature seems to be necessary to reproduce both VLE and SLE data for this system and other

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systems containing compounds with functional groups in common with the acetic acid + water system.

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parameterization of the thermodynamic model AIOMFAC: calculation of activity coefficients for organic-inorganic mixtures containing carboxyl, hydroxyl, carbonyl, ether, ester, alkenyl, alkyl, and aromatic functional groups, Atmos. Chem. Phys., 11, 9155–9206, doi:10.5194/acp-11-9155-2011, 2011.

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Revised caption to Fig. 1 (see next page): Database distribution for the water ↔ organic and organic ↔ organic interaction parameters. The table lists for each main group interaction pair at temperatures substantially different from the reference temperature, $T_{\ominus} = 298.15$ K, i.e., per dataset d : $T_{d,low} < 289$ K or $T_{d,high} > 307$ K, the following information. Top boxes: the total number of datasets available, visualized by the green bars. Middle boxes: the lowest temperature (T_{low}) and the highest temperature (T_{high}) (units of K) of the data points using a percentile-wise colour scale. Bottom boxes: the median and arithmetic mean of the assigned initial dataset weighting values (w_d^{init}) of the datasets involved.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 16907, 2014.

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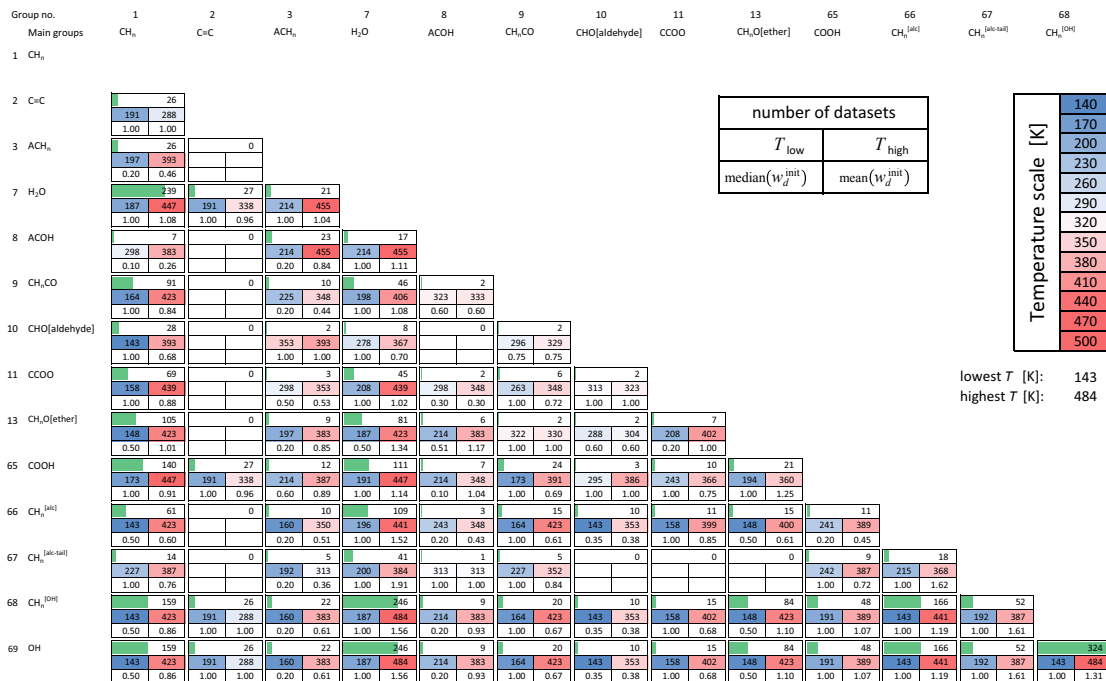


Fig. 1.

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