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Atmospheric Chemistry and Physics
Discussions

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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This is a thorough work extending the scope of the AIOMFAC model even further. A lot of data is collected and new measurements are performed. The work is well written. Nonetheless, there are several, mostly minor, points which have to be addressed or clarified before publication in ACP.

1 General points

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 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.

2 Specific points

1. Abstract, page 16908, line 25. 'overall improvement of 25%'. As an abstract should stand on its own, you have to clarify here in what exactly the method has improved.
2. 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.

3. Page 16911, line 25-26. State clearly if this is absolute or relative uncertainty.

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

5. 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?

6. Page 16912, line 24. For clarity, state explicitly which AIOMFAC functionalities are not considered.

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

8. Page 16914, line 9. Please clarify that these groups where introduced from Compernolle et al. (2009).

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

10. 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?

11. 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.

12. 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?

13. 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.

14. 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.

15. Page 16924, line 22. What does ’forward computation’ mean in this context?

16. 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?

17. 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?
18. Page 16929, line 5-6. Define $T_{\text{low}}, T_{\text{high}}$.
19. 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.
20. Page 16929, line 20. On which basis have these particular limits been chosen?
21. 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 $F_{\text{obj,low}}$) and well above room temperature (giving rise to $F_{\text{obj,high}}$). For people interested in organic aerosol mixtures, especially the improvement in $F_{\text{obj,low}}$ will be of interest.
    (c) In the same spirit, F_{obj} should be split over $F_{\text{obj,mono}}$ and $F_{\text{obj,poly}}$, referring to data for monofunctional and for polyfunctional compounds respectively. Is there a significant improvement in $F_{\text{obj,poly}}$, which is probably of most relevance to aerosol mixtures ?
22. 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 $F_{\text{obj,poly}}$: is there a significant improvement for polyfunctional compounds specifically?

23. 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.
24. This could be an argument that for significant further improvement, also the a_{mn} parameters should be reparametrised. Could the authors comment on this?
25. Table 1, caption. Mention that the data with $w_d^{\text{init}} = 0$ do not affect the reparameterization.
26. Figure 1, caption. Define here what 'substantially different' means.

3 Technical corrections

1. Page 16910, line 19. "...(SLE) data, following the...". Replace the komma by a point.
2. Page 16911, line 8. Remove "often".
3. Page 16922, Eq (19). In general there can be multiple transition points. So a sum over transition points would be more appropriate.
4. Page 16923, line 7-8. Put both references in one set of brackets.

5. 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.

6. 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)?

References

Compernolle, S., Ceulemans, K., and Müller, J.-F.: Influence of non-ideality on condensation to aerosol, Atmos. Chem. Phys., 9, 1325–1338, 2009.

Zuend, A., Marcolli, C., Booth, A. M., Lienhard, D. M., Soonsin, V., Krieger, U. K., Topping, D. O., McFiggans, G., Peter, T., and Seinfeld, J. H.: New and extended 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.

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