

Interactive comment on “A thermodynamic model of mixed organic-inorganic aerosols to predict activity coefficients” by A. Zuend et al.

Anonymous Referee #3

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The authors present a modified LIFAC activity coefficient model for calculating non-ideality in systems involving common inorganic salts and a wide range of alcohols and polyols. By introducing a semi empirical middle range parameterisation of direct organic-inorganic interactions in alcohol+water+salt systems results are improved considerably.

The use of functional groups within any predictive framework gives end users the opportunity to analyse systems which may harbour organics not necessarily used during the parameter fitting procedure. This in itself is advantageous over compound specific models. However, there seems to be an interesting tradeoffs between flexibility and overall accuracy. Ultimately for atmospheric purposes we may have to rely more heavily on functional group methods which are continually improved on an ever expanding

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database.

Overall I think the paper reads very well and provides the community with yet another thermodynamic model with an aim to more fully understand mixed inorganic/organic aerosols and their role in the environment.

I have some general and minor comments below:

General comments:

My first general comment revolves around the restricted range of functional groups used in the first instance. The UNIFAC concept in some way centres around the use of as much data as possible for deriving interaction parameters. I fully understand you are somewhat limited in this instance with available data. However, by fitting parameters for systems involving only alcohols/polyols and inorganic salts, do you have a feel for whether activity coefficient predictions would be more accurate than assuming inorganic-organic interactions are zero when this model is used for systems involving CH_n and OH but not as polyols/alcohols? Presumably this would require more testing but models such as those presented here become benchmarks for the wider community.

Secondly, you have presented an alternative method, albeit using the LIFAC framework, for calculating activities in aqueous inorganic mixtures. Interestingly you make the comment that, for the majority of systems, an adequate level of accuracy is obtained by neglecting ternary and higher order interaction terms. The community as a whole currently relies on the very accurate yet computationally expensive AIM equilibrium model which houses the Pitzer-Simonson-Clegg activity coefficient model for inorganic ions. I would imagine that AIOMFAC will be used as a benchmark code comparable to E-AIM. If so, would you suggest that added numerical complexity such as the addition of ternary interaction parameters is largely unnecessary or simply impractical?

In AIOMFAC to account for LLE you use water as the reference solvent in all cases and

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account for discrepancy between this assumption and actual behaviour through the introduction of semi empirical mid-range interaction terms. However, for very dilute solutions where these mid-range terms become else significant, will this make AIOMFAC less or more suitable than say a ZSR approach?

You mention that in your model aqueous electrolyte solutions are described in a similar manner as in a conventional Pitzer model. Does this place a concentration limitation on your framework? In other words, could someone expect predictions to deviate wildly beyond the concentrations ranges used in fitting the interaction parameter basis sets.

Related to the above question. If you analyses systems which do not contain the inorganic ions and organic functional groups used in this study, what does AIOMFAC converge on? i.e. would it give the same predictions as if one were using the Pitzer-Simonson-Clegg activity model for inorganic ions and UNIFAC for the organic fraction?

Have you compared your approach with E-AIM for the systems studied, or at least do you plan to? This would be interesting in itself as this model uses a slightly different approach than that provided here. Could you comment on the comparable applicability of both?

Minor revisions:

Page 6092 line 12. replace '‘own measurements’' with '‘our own measurements’';

Page 6098 line 1. replace '‘are describing’' with '‘predict’';

Page 6104 line 24. remove '‘often’';

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 6069, 2008.

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