

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

**A. Zuend et al.**

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The authors would like to thank anonymous referee #3 for his/her review and valuable comments.

We have addressed the referee's concerns point-by-point below.

### **Replies concerning the referee's 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 interactions parameters. I fully understand you are somewhat limited in this instance with available data. However, by fitting

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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<sub>n</sub> 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.

*Reply:*

Our parametrisation of the OH and CH<sub>n</sub> groups is very comprehensive because we used activity data of many different alcohols and polyols. Typically, only simple alcohols are used to parametrise OH. However, we have still to check how well this parametrisation procedure can be extended to further functional groups. With our stepwise approach, there is a certain risk that we will have to reparametrise the MR interactions of CH<sub>n</sub> and OH with ions, to successfully implement further functional groups. One intention of this study was to show the applicability of our framework.

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 interactions parameters is largely unnecessary or simply impractical?

*Reply:*

Terms between e.g., two different cations and an anion are in general impractical because data of ternary solutions is required to estimate the interaction parameters. Our aqueous multi-salt solution examples also show that such terms are in general

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not needed. For the different ammonium sulphate–sulphuric acid mixtures, a ternary cation–cation–anion interaction coefficient was needed to obtain good agreement with data of highly concentrated solutions. This example shows that there are certainly some exceptions, where ternary interaction terms are required.

In AIOMFAC to account for LLE you use water as the reference solvent in all cases and 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 less significant, will this make AIOMFAC less or more suitable than say a ZSR approach?

*Reply:*

AIOMFAC shows good agreement with measurements for very dilute aqueous solutions (see e.g., Fig. 5 and 6 for  $x_w$  close to 1.0). It is as good as a ZSR approach without the limitations of the ZSR concept (see e.g., Fig. 6a).

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.

*Reply:*

In the figures, we show the AIOMFAC results over the whole concentration range. In the range where experimental data is available, the agreement is as good as in AIM III (see e.g., Fig. 11). At higher concentrations our predictions are thermodynamically consistent extrapolations. We reached this good performance at high electrolyte concentrations by introducing an additional middle-range interaction coefficient,  $C_{c,a}(l)$ , and by placing a constraint on the slope of the  $a_w$  curve.

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Related to the above question. If you analyse 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?

*Reply:*

It would give a similar quality of prediction.

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?

*Reply:*

E-AIM does not contain organic–inorganic interaction parameters and would therefore perform similarly as if in AIOMFAC these were set to zero. Thus, salting-in and salting-out effects can not be described. These effects play an important role in alcohol–water–salt solutions.

### Replies concerning the referee's minor revisions

We changed the minor revisions as suggested.

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

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