Atmos. Chem. Phys. Discuss., 11, C5772–C5776, 2011
www.atmos-chem-phys-discuss.net/11/C5772/2011/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "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" *by* A. Zuend et al.

Anonymous Referee #1

Received and published: 30 June 2011

The authors present a major extension of the model AIOMFAC, enabling the calculation of activity coefficients of water-organics-salt mixtures. The scope of the method entails a considerable variety of organic functional groups and inorganic ions, making it a valuable tool for explicit chemical models for aerosols. A large and diverse set of experimental data was gathered, new measurements were performed where these data was lacking, and substantial technical challenges were overcome regarding parameter optimization. The authors also do a good job in explaining systematically and clearly

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

a complex subject, and provide a lot of material. I therefore recommend publication in ACP.

General comments

My only important remark is on the use of the existing UNIFAC parameters, assembled from different research groups, for describing the organic-organic and organic-water interactions. The authors have stressed the importance of fitting the organic-ion interaction parameters for all data simultaneously. Shouldn't the same be true for the organic-organic and organic-water interactions, i.e. wouldn't it be better to refit these parameters over a wide variety of mixtures at once? The authors point to the shortcomings of the UNIFAC model in some circumstances, even for salt-free systems, and blame this solely on the group-contribution concept. But I think there can be another reason: the fact that the UNIFAC set of interaction parameters is not obtained by an overall optimisation. It would make sense to me -if time and manpower would be no limitation- to first have the optimal UNIFAC parameters for a best description of salt-free mixtures, before improving/extending the organic-ion interaction parameters. Have the authors refrained from this because of the challenge of the task, or do they think that the existing UNIFAC parameters cannot be much improved upon?

The complexity of UNIFAC/AIOMFAC stands in sharp contrast with the simple one of Donahue et al. (2011). This model only aims to model the overall aerosol properties, not the individual components. Can this simple model be sufficient to predict e.g. phase separation in aerosol, or do the authors think that a detailed model such as UNIFAC/AIOMFAC is indispensable for this?

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Specific comments

p. 15306, line 13. The authors use parameters from Peng (2001), but the UNIFAC model of Raatikainen (2005), described for the same compound types (diacids and hydroxy acids), is based on a larger and more diverse data set. Is there a reason why the parameter set of Peng was preferred over that of Raatikainen?

p. 15307, line 3-5. The $\mathrm{CH}_n^{(\mathrm{OH})}$ group leads to a better description of alcohols, polyols and sugars. But the authors should also mention other molecules with hydroxy groups. What about e.g. hydroxy acids and hydroxy ketones? For example, citric acid is within AIOMFAC described by parameters from original UNIFAC, UNIFAC-Peng and UNIFAC-MP. I could imagine that its description will be less optimal than by UNIFAC-Peng only.

p. 15313, Eq. (9) and following text. w_d^{init} is determined based on data type and temperature range, but how exactly? Did you apply some protocol or was it simply chosen by intuition?

p. 15316, Eq. (11). C=C is also in the first series, while it has two carbon atoms. Shouldn't it be removed from this first series?

Same equation. Is it possible to locate a zero-point (refering to water) in both series?

p. 15319, Eq. (13). I am a bit surprised to see a *difference* of activity coefficients here, instead of a ratio (or a difference of their logarithms). Normally it is the logarithms of activity coefficients that are added, e.g. the functional group activity coefficients in the UNIFAC model to obtain the molecular activity coefficient, or the weighted average of $\ln \gamma_i$ to obtain the Gibbs molar excess energy. Was a difference of logarithms also tried, and was the current approach found to be superior?

p. 15320, line 9. Can the “+1” term be derived mathematically, or was it artificially introduced?

p. 15320, last line and first line of 15321. You could show the formula how to calculate

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

y1 with AIOMFAC. Is for this data type (x-y-T data without p) no isolation of the salt-effect attempted?

Section 4.3. It was not completely clear to me how the LLE data are taken into account:

- p. 15323. line 21. "set to the activity value". I guess that from LLE data one only has the concentrations in both phases, not the activities. One only knows that the activities have to be the same in both phases. So is the "activity value" here obtained by using the experimental concentrations and the AIOMFAC calculated activity coefficient?
- p. 15323, line 24. "rel. activity devation". It is not clear to me how this quantity is defined. Is it defined as $\frac{a_j^{\beta}-a_j^{\alpha}}{a_j^{\alpha}+s_j^{a,\alpha}+s_j^{a,\beta}}$, where concentrations are experimental and activity coefficients are calculated by AIOMFAC?
- p. 15323, line 23. The sensitivities for both phase activities are summed. Shouldn't it be $\sqrt{\left(s_j^{a,\alpha}\right)^2+\left(s_j^{a,\beta}\right)^2}$ according to the error propagation rule for sums?
- p. 15323, line 25. "The absolute values of the relative activity deviations ... are calculated relative to". Shouldn' the first "relative" be scrapped here?

p. 15336, line 15. I think that also the molecule classes "hydroperoxides" and "nitrates" should be added as to be beyond the scope of UNIFAC, at least as long publicly accessible parameters are meant. Do the authors have any recommendations when such molecule classes are encountered? E.g. working by analogy (e.g. treat hydroperoxides as alcohols), or simply ignoring non-ideality for such compounds?

p. 15337, line 8 "However, it is at present not possible to provide a quantitative estimate of how well AIOMFAC will perform for mixtures that were not part of the database used for the parameter determination." Why is this not possible? One could for example split the dataset into two, using one part as the fitting set and the other part as the test set to test the predictive capacity of the model.

Minor comments

p. 15329, line 13. "theses" should be "these"

Fig. 6, caption. "(Chiavone-Filho and Rasmussen, 1993)" should be "Chiavone-Filho and Rasmussen (1993)".

References

Donahue, N. M., Epstein, S. A., Pandis, S. N., and Robinson, A. L.: A two-dimensional volatility basis set: 1. organic-aerosol mixing thermodynamics, Atmospheric Chemistry and Physics, 11, 3303–3318, 2011.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 15297, 2011.