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Atmospheric
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Discussions

Interactive comment on "Application of several activity coefficient models to water-organic-electrolyte aerosols of atmospheric interest" *by* T. Raatikainen and A. Laaksonen

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We would like to thank referee for useful comments. Answers are given after the referee comments.

Responses to the specific comments

1. The original UNIFAC is common for all the models presented. I would definitely suggest the use of UNIFAC Dortmund (Gmehling at al, Ind. Eng.Chem.Res 32, 178-193, 1993), given its higher reliability; the intermolecular interactions are better reproduced and takes into account the differences in the molecular sizes. Also the temperature *dependence is more accurately expressed. A very important characteristic for UNIFAC Dortmund is that the activity coefficients at infinite dilution can be predicted.*

There are three main reasons why the original UNIFAC was selected instead of Dortmund UNIFAC. The first reason is that there are less fitting parameters in the original UNIFAC. Dortmund UNIFAC has three interaction parameters (UNIFAC only one), which makes fitting process much more difficult. The second reason is that most of our fitting data was available at temperatures close to 298 K. Then these two extra interaction parameters can be quite useless. The third reason is that the Dortmund UNIFAC is especially suitable for infinite dilution activity coefficients, but our main purpose is predicting water activities (referee's question 3). Furthermore, to be able to accurately predict organic activities at infinite dilution, we would have needed more organic (infinite dilution) activity data, which was not available. In the future, it would be interesting to test Dortmund UNIFAC (or some other UNIFAC version) for non-electrolyte and electrolyte solutions.

2. The work of Aznar and Teller presented in Braz. J. Chem. Eng 18. 2001 presents the prediction of electrolyte vapor-liquid equilibrium by UNIFAC-Dortmund only, by dropping the Debye-Huckel and estimating instead group interaction parameters for ions and between ions and solvent groups. The results are in fairly good agreement with the experimental data and by eliminating the DG for ion-ion interaction, the fitting and modelling work is reduced substantially. Probably the authors should consider this approach also, at least when comparing their modified predicted models with the existing ones.

The model of Aznar and Telles (2001) is similar to our fitted UNIFAC model. Both models are suitable for predicting solvent activities in electrolyte and non-electrolyte solutions, but modelled organics are different. Furthermore, Aznar and Telles consider salts as non-dissociating species, which are composed of ions as functional groups. This is not possible in our version of UNIFAC, because our other models, where ion activities are calculated, use these same UNIFAC parameters. Question about preferring the Dortmund UNIFAC to the original UNIFAC reduces to the referee comment 1.

The simple Debye-Huckel term has no fitting parameters, only pure component properties (density, molecular weight,...), so it has only a small effect to fitting and modelling.

In the model comparison, we compared the original UNIFAC with our UNIFAC using non-electrolyte data (Table 5). Original UNIFAC had much bigger deviations than the models fitted for this kind on of mixtures, so it is not likely that the Aznar and Telles model would be better. Aznar and Telles model is not suitable for predicting electrolyte activities, and it not likely that the model would have been accurate for organic-electrolyte mixtures used in the model comparison, because Aznar and Telles did not used these compounds in parameter fitting. There are also many other models that we could have used in model comparison (other versions of UNIFAC, original organic-electrolyte models (LIFAC), etc.), but our article is already quite long and this would have increased the length even more.

3. The models behavior at infinite dilution is not extensively presented.

The main purpose of the fitted models is predicting water activities in aqueous organic-electrolyte solutions. Because the biggest problem in parameter fitting was lack of organic activity data, these models may not be suitable for predicting infinite dilution activity coefficients. The only organic activity data was activity in saturated solution, which was calculated using melting enthalpies. Models suitability for infinite dilution activity coefficients will be clarified in the final version of our article.

If the referee meant model's reference states, these are explained in the original articles and briefly in the appendices.

4. Part of the available experimental data should be for comparison purposes only,

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without being included in the fitting part in order to test the reliability of the model prediction. If the authors proceeded so, they should present the result accordingly, specifying the mixture(s) and presenting the results separately.

Some of the experimental data was left for model comparison only. For example, there are some data sets of non-electrolyte data, which was not used in the fitting. However, the lack of data was the biggest problem in the fitting so most of the experimental data sets were used. Because most of the experimental data, including the "best" data sets, was used in the fitting, it was decided to use all data sets in model comparison. The main tests for model reliability were comparison with each other, with other published models and calculation of growth factors for organic-salt particles. If we would have fitted only one model, it would have been easy to handle all data set individually, but in this case, it would have caused too long article.

5. In the atmospheric science, not only the water activity is important, but also the activities for the other components, i.e. the organics. Such experimental data can be found in literature and can be compared with the UNIFAC presented here. This can be considered a test for the accuracy of the new fitting parameters.

If more organic activity data had been found, it would have been used in the fitting. Unfortunately there are very few data available and some of the data could not be used here (e.g. different reference state). The only comparison that was made is solubility calculations in Table 5, where our predictions were compared with Ming & Russell model, original UNIFAC and Peng et al. (2001) UNIFAC.

Responses to the technical corrections

6. page 3643, lines 22-23. Add reference for the 50% of the aerosol dry

Reference Chow et al., 1994 will be added to the final version

7. page 3647, line6. Add the word 'subscript' between the brackets for c - cation and a -anion. 'a' has been used before for representing the activity.

This will be fixed to the final version.

8. page 3649, r18: there exist -> there exists

This will be fixed to the final version.

9. page 3651, lines 10-11. You should explain here, at this point, why you used the 30 mol/kg limitation and not in the appendix.

Explanation will be added to the final version.

10. page 3656, line 5. The authors said that Ming and Russel model is one the few activity coefficient models for atmospheric mixtures. In such case what other models exist and why they have not been used in this work?

Ming and Russell model and ADDEM (Topping et al., 2004) are the two published activity coefficient models for atmospheric mixtures, which were included in the model comparison. There are also models for mixtures of electrolytes and organic solvents (e.g. original LIFAC), but usually organic solvents (e.g. ethanol) are not common in the atmosphere. Furthermore, there are methods, where activity coefficients of species in multicomponent mixture are calculated from binary data and with or without mixture parameters (e.g. Clegg et al., 2003, J. Aerosol Sci., 667-690). For clarity of the tables and figures, only few of the published models could be taken to the model comparison. We will clarify this in the final version.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 3641, 2005.