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Atmospheric
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Discussions

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 #2 for his/her detailed review and valuable comments.
We have addressed the referee's concerns point-by-point below.

Replies concerning the referee's specific comments

Page 6072, line 12: The term group-contribution method could be explained simply by comparing UNIFAC and UNIQUAC models. UNIQUAC should be referenced.
Reply:
We replaced in the revised manuscript version the sentence starting with "For or-

ganic systems,..." by: "For non-electrolyte liquid mixtures, the substance specific UNIQUAC (UNIversal QUAsi-Chemical) model (Abrams and Prausnitz, 1975) and its group-contribution version UNIFAC (UNIquac Functional group Activity Coefficients) (Fredenslund et al., 1975) are widely used for the prediction of liquid-phase activity coefficients of organic species and water."

Page 6072, line 23: In addition to the section 3.4, the authors could comment on the other organic-inorganic models designed for aerosol modelling.
Reply:
In the introduction, we just wanted to focus on the models AIOMFAC is based on (UNIFAC, LIFAC). Therefore we do not mention other models designed for aerosol modelling at this point. However, as suggested below, we extended section 3.4 to include additional activity coefficient models for comparison with our model.

Page 6074, section 2.1.1.: Group contribution concept comes from the original UNIFAC (not from LIFAC) and the model includes also water (water should not be connected to ions). The group contribution concept was extended for electrolyte solutions, when ions were included to LIFAC. AIOMFAC is based on LIFAC.
Reply:
We changed the first sentence in section 2.1.1 to: "Following the idea of UNIFAC, a group-contribution concept is used to describe interaction effects of organic compounds and water in a solution, thereby covering a large number of organics by means of just a few functional groups."
The first two sentences in the second paragraph were replaced by: "The group-contribution concept can be extended to electrolyte solutions by the inclusion of ions as put forward by e.g., extended UNIFAC or the LIFAC models. AIOMFAC is based on LIFAC and uses the same group-contribution concept."

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Page 6083, line 19: Are the UNIFAC expressions (equations) modified or are just parameters modified? This should be clarified.

Reply:

The UNIFAC expressions (equations) were not modified, only the parameters and the way an alcohol is composed of the different subgroups. We replaced the word “expressions” by “parametrisations”.

Page 6083, line 23: These interaction parameters should be described shortly, because they are not given in this paper.

Reply:

We replaced the sentence starting with “In this way,...” by the following short description of the used parametrisation: “This UNIFAC parametrisation of alcohols/polyols distinguishes between three types of alkyl groups: (i) $\mathrm{CH_n}$ (n=0, 1, 2) with a hydroxyl group, accounting for the induced polarity of alkyl groups directly connected to the electronegative hydroxyl group, (ii) $\mathrm{CH_n}$ (n=0, 1, 2, 3) in hydrophobic tails, accounting for the non-polar nature of alkyl chains that easily agglomerate and form micelles in water, and (iii) $\mathrm{CH_n}$ (n=0, 1, 2, 3) in alcohols, which constitutes the general type of alkyl group that applies when the special conditions for the other two types are not fulfilled.”

Page 6084, lines 1-2: This argument needs an explanation. One could expect that relative distance has more to do with the size parameters.

Reply:

See above.

Page 6092, line 12 and page 6094, line 20: Both bulk water activity and EDB measurements should be described in a separate section or at least in Appendix A.

Reply:

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We changed the sentence on page 6092 to: “A description of the experimental procedure and the measured water activities are given in Appendix A.”
In Appendix A the following paragraphs were added: “Tables A1 and A3–A9 show data of our own water activity measurements at room temperature using an AquaLab water activity meter (Model 3TE, Decagon Devices, USA) for bulk measurements. This instrument allows us to perform measurements in the temperature range from 289 to 313 K. The inorganic aqueous electrolyte solutions were measured with the standard sample block, for which an accuracy of ± 0.003 a_w is specified by the manufacturer. For the measurements of organic–inorganic mixtures containing polyols, the volatile sample block available as an accessory to the instrument was used. With this sample block, the water activity in the presence of other semi-volatile components can be determined. Experimental errors for the volatile sample block are specified to be ± 0.015 a_w. To correct for instrument drifts and offsets, the performance of the sample block was frequently controlled and readjusted with reference samples. All measurements were performed at 298±1 K. The operating principle of this instrument is described in more detail in Marcolli and Peter (2005) and Marcolli and Krieger (2006).

The inorganic salts were purchased from Sigma-Aldrich with purities of 99% or higher. Sulphuric acid was purchased from Merck with a concentration of 96.06%. The polyols were purchased from Fluka with purities ranging from $\geq$95% to $\geq$98% ($\geq$95%: 1,7-heptanediol, 1,2,4-butanetriol; $\geq$97%: 2,5-hexanediol; $\geq$98%: 1,2-butanediol, and 2,4-pentanediol). The substances were used without further purification. The solutions were prepared by mass percent with ultrapure water (Millipore Simplicity 185) using an analytical balance. The compositions of the aqueous electrolyte solutions were corrected to include the water which was present in the salts as purchased.

Table A2 shows water activity data from our EDB measurements. The electrodynamic balance used in our experiments is described in detail elsewhere (Colberg et al., 2004; Marcolli and Krieger, 2006). An electrically charged particle (typically 2-7 μm in radius) is balanced in an electrodynamic trap where the temperature is kept constant and the relative humidity within the EDB-chamber is increased or decreased continuously by changing the N_2/H_2O ratio in the gas phase, using automatic mass flow controllers. The relative humidity is registered by a sensor in the trap with an accuracy of $\pm 1.5\%$ RH between 10 and 90% RH. The mass of the particle is calculated from the DC voltage compensating the gravitational force. A change in DC voltage is therefore a direct measurement for the mass change of the particle. The experiments in the EDB were performed at 288 K. The measured ammonium sulphate–sulphuric acid solutions were prepared with the same procedure as for the AquaLab bulk measurements."

Page 6097, line 17: The authors write that higher order interaction parameters are ignored. Is the sulphuric acid-ammonium sulphate mixture the only exception? For example sulphuric acid-ammonium chloride solution contains the same ions.
Reply:
The only exceptions so far are systems containing the ion combinations NH_4^+, H^+ or NH_4^+, H^+, SO_4^{2-}. Thus, sulphuric acid–ammonium chloride solutions are among those exceptions. We clarified this issue by replacing the words "... containing sulphuric acid and ammonium sulphate, ..." on page 6080, line 9 by "... containing the ion combinations NH_4^+, H^+ or NH_4^+, H^+, SO_4^{2-} (e.g., sulphuric acid–ammonium sulphate solutions), ...".

Page 6099, starting from line 10: It seems that the authors have just calculated activities by using experimental LLE data (equilibrium composition). Usually equilibrium composition is the unknown which is calculated by using activity coefficient models. Because current model should be applicable to LLE calculations, some calculations should be done and model predictions should be compared with experimental values.
Reply:
LLE data (measured equilibrium compositions) were used to enhance the data base for model parameters estimations and for conceptual consistency, in a future paper

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AIOMFAC predicted LLE will be shown.

Page 6101, line 14: It looks like the actual model comparison starts at this line (should start new paragraph). Model comparison is focused on salt solutions, but also inorganic-organic and non-electrolyte solutions should be mentioned. When comparing models, it should be kept in mind that models have different types of organics (from solvent-like to poorly soluble). Partly for this reason, models are used for different calculations (LLE, VLE, SLE). Also, the availability of fitting data depends on the solutes. Lack of data may be the biggest problem in the modelling of atmospherically relevant mixtures. Some other models could be mentioned here, e.g. substance specific models are not commented at all. In addition to the mod. LIQUAC (UNIQUAC version of the mod. LIFAC), extended UNIQUAC (Thomsen, K, Iliuta, M.C., Rasmussen, P.: Extended UNIQUAC model for correlation and prediction of vapor–liquid–solid equilibria in aqueous salt systems containing non-electrolytes. Part B. Alcohol (ethanol, propanols, butanols)–water–salt systems, Chem. Eng. Sci., 59, 3631-3647, 2004) could be mentioned.
Reply:
In Fig. 11 we compare model predictions for inorganic solutions, Figures 12 and 13 show comparisons for organic–inorganic mixtures. Non-electrolyte solutions were not compared since in these cases AIOMFAC reduces to the UNIFAC version of Marcolli and Peter (2005). AIOMFAC will then be typically less accurate compared to substance specific UNIQUAC models.
We inserted the following sentences at page 6101, line 14, to explain why we only compare group-contribution models with AIOMFAC: “Atmospheric aerosols contain a large number of often poorly characterised organic compounds, which are dominated by a relatively small number of functional groups. This circumstance favours group-contribution models over substance specific models when used for aerosol modelling. Keeping this in mind, we focus here on the comparison of AIOMFAC with other group-contribution activity models rather than on a comparison with substance

specific organic–inorganic activity models like extended UNIQUAC (Thomsen et al., 2004) or mod. LIQUAC (Kiepe et al., 2006).”

Page 6102, lines 3-17: The points of these two paragraphs should be clarified. Different models have different UNIFAC parameters, because model organics are different.
Reply:
We changed the sentence “In contrast to ...” starting on page 6102, line 12 to: “In contrast to the other models with a UNIFAC part, AIOMFAC includes the new UNIFAC parametrisation by Marcolli and Peter (2005), which represents better the SR contribution of alcohols/polyols found in atmospheric aerosols.” The following sentence “Methods based on ...” now starts a new paragraph.

Page 6105, line 4: Water activity and EDB measurements need better description.
Reply:
These measurements are now described in Appendix A (see above).

Page 6146, Fig. 8 and page 6150, Fig. 12c: Water activity exceeds unity, this should be commented.
Reply:
We added the following sentence on page 6099, line 9, where Fig. 8 is discussed: “Note that in the panels (b) and (d) of Fig. 8 the predicted salt-free solution curves show water activities exceeding 1.0 because we did not allow for the formation of a LLE in the model calculations.”

Replies concerning the referee’s technical corrections

Page 6072, lines 11-15: The sentence starting “For organic systems, the UNIFAC model” should be clarified.
Reply:
See the reply to the first specific comment.

Page 6073, line 8: Supersaturated bulk solutions are also possible.
Reply:
We agree. The sentence was changed to: “Compared with bulk solutions, in liquid aerosol droplets much higher supersaturations (metastabilities) with respect to crystalline phases can be reached.”

Page 6073, line 12: Is the EDB data measured by the authors? If yes, it should be mentioned.
Reply:
Mainly literature data of EDB measurements is used (one exception).

Page 6078, line 11, equations 11 and 12: Static permittivity is presumably relative static permittivity (no unit).
Reply:
Right. We changed this in the revised manuscript.

Page 6095, section 3.2: This title could refer to electrolyte solutions.
Reply:
We agree and changed the title in the revised manuscript.

Page 6097, line 21: The word “und” should be “and”.
Reply:

Changed.

Page 6101, line 18: Significant fractions of published models are valid for concentrations up to solubility limit, which is rarely a dilute solution.

Reply:

We changed the sentence to: “Most other models are limited to the concentration range of dilute to, at maximum, saturated electrolyte solutions.”

Page 6102, lines 21-22: Are the water activity differences or just predicted water activities in good agreement?.

Reply:

We changed the sentence to: “Panels (a), (b), and (c) of Fig. 11 show that the water activities calculated by AIM III and AIOMFAC are in good agreement with the measurements up to high salt concentrations (a_w<0.6).”

Page 6103, line 2: If the mod. LIFAC is not designed for SLE calculations, it can not be expected that the model predicts correct activity coefficients for highly supersaturated solutions. Different predictions (panel c) may also be caused by different experimental fitting data or differences in model parameters (e.g. rounding errors).

Reply:

We added the following sentence to explain part of the behaviour of mod. LIFAC: “Because mod. LIFAC was not parametrised for supersaturated electrolyte solutions, such artefacts can appear for predictions of highly concentrated (supersaturated) solutions.”

Page 6103, line 12: VLE activity coefficient or just activity coefficient?

Reply:

We changed the sentence to: “Panels (a) and (b) of Fig. 12 show two examples of activity coefficient comparisons for isobaric VLE data.”

Page 6105, line 4: Word “our” could be better than “own” in the first sentence.
Reply:
Changed (see above).

Page 6105, References: Sometimes symbol “+” is replaced by word “plus”. Brenner et al. (1992): Check the title, Chan et al. (1992): Journal title should be Atmos. Environ., Li et al. (1994): Check the title.
Reply:
We checked again the list of references and replaced the words you mentioned and some other misspellings in titles.

Page 6119, Table 3: What is the first character in the line right after ammonium bisulphate? Does it mean that ammonium bisulphate is equal to the 1:1 mixture of ammonium sulphate and sulphuric acid? There is no that kind of explanation for sodium bisulphate.
Reply:
The aim here is mainly to show and denote the different ammonium sulphate–sulphuric acid mixtures, therefore the 1:1 mixture for ammonium bisulphate is denoted. For consistency we indicated now also the 1:1 mixture of Na_2SO_4 + H_2SO_4 in the case of $NaHSO_4$.

Page 6140, Fig. 2: Why groups CH_n-CO, COOH and CH_n-O are included in the table? They are not mentioned in the text.
Reply:

We added those functional groups to Fig. 2 because they are important organic groups found in the compositions of atmospheric aerosols. In the revised manuscript we added the following sentence to the figure caption: “CH_n-CO, COOH, and CH_n-O present further important organic main groups whose MR interaction parameters are not estimated so far.”

Page 6084, line 8: If the original equations are used, the citation should be changed.
Reply:
Yes the original equations are used. Citation changed to (Fredenslund et al., 1975).

Page 6141, Fig. 3: Figure contains a lot of data. It is readable, but it could be bigger. Same comment for Figures 4, 5 and 6. Figures 10 and 12 are also quite full.
Reply:
We are aware of the fact that some figures are quite full, but we hope that in the final ACP version they will be printed two columns wide and larger. The figures are vector graphics and thus lossless scalable in the electronic version.

Page 6129, Table A1: Some words are missing from “Concentrations of the electrolytes are given fractions”.
Reply:
It should be: “Concentrations of the electrolytes are given in mass fractions.”

Page 6148, Fig. 9: Figure caption should be clarified. LLE is not calculated here, because composition values are from experiments.
Reply:
To clarify this, we replaced the first to sentences by: “Plots of the relative activity deviations between the two coexisting phases of alcohol–water–NaCl mixtures in LLE

at 298 K.”

Page 6148, Fig. 10: Figure 10a contains activity coefficients, not VLE.
Reply:
We replaced the first sentence by: “(a) activity coefficients of isobaric 2-propanol–water–NaBr mixtures in VLE at 353–358 K.”

Page 6151, Fig. 13: Label of the horizontal axis “mixture No. (of coexisting liquid phases)” could be better. LLE is mentioned in the caption, but this equilibrium is not calculated.
Reply:
We agree that the label of the horizontal axis is somewhat ambiguous and therefore we replaced the labels in Fig. 9 and 13 by “mixture No.” . The first sentence in the caption was changed to: “Comparison of mod. LIFAC and AIOMFAC calculations for different alcohol–water–salt mixtures in LLE at 298 K.”

References

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