

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

Anonymous Referee #2

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Zuend et al. present a new version of a predictive organic-inorganic activity coefficient model. Unlike the previous model versions, this new version is suitable for solid-liquid, vapour-liquid and liquid-liquid equilibrium calculations. Selected ions include most of the atmospherically relevant ones. Organics are alcohols and polyols. The model seems to be especially accurate for single and mixed electrolyte solutions even for concentrations well above saturation. Deviations are slightly bigger for organic-inorganic mixtures, but still reasonable. In addition to the model, the paper contains new water activity data for aqueous mixed electrolyte and polyol-electrolyte solutions. The paper is also well written. I recommend this paper for publication after a few corrections.

Specific Comments

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Page 6072, line 12: The term group-contribution method could be explained simply by comparing UNIFAC and UNIQUAC models. UNIQUAC should be referenced.

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

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.

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

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

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

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

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.

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.

Page 6101, line 14: It looks like the actual model comparison starts at this line

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(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.

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.

Page 6105, line 4: Water activity and EDB measurements need better description

Page 6146, Fig. 8 and page 6150, Fig. 12a: Water activity exceeds unity, this should be commented

Technical Corrections

Page 6072, lines 11-15: The sentence starting "For organic systems, the UNIFAC model" should be clarified.

Page 6073, line 8: Supersaturated bulk solutions are also possible.

Page 6073, line 12: Is the EDB data is measured by the authors? If yes, it should be mentioned.

Page 6078, line 11, equations 12 and 12: Static permittivity is presumably relative static permittivity (no unit)

Page 6095, section 3.2: This title could refer to electrolyte solutions

Page 6097, line 21: The word "und" should be "and"

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

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

Page 6103, line 2: If the mod. UNIFAC 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).

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

Page 6105, line 4: Word "our" could be better than "own" in the first sentence

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

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.

Page 6140, Fig. 2: Why groups $\text{CH}_n\text{-CO}$, COOH and $\text{CH}_n\text{-O}$ are included in the table? They are not mentioned in the text.

Page 6084, line 8: If the original equations are used, the citation should be changed

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.

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Page 6129, Table A1: Some words are missing from "Concentrations of the electrolytes are given fractions";

Page 6148, Fig. 9: Figure caption should be clarified. LLE is not calculated here, because composition values are from experiments

Page 6148, Fig. 10: Figure 10a contains activity coefficients, not VLE

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.

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