

Interactive comment on “Computation of liquid-liquid equilibria and phase stabilities: implications for RH-dependent gas/particle partitioning of organic-inorganic aerosols” by A. Zuend et al.

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The authors would like to thank referee #2 for the consideration and careful review of the manuscript and valuable comments.

We have addressed the reviewer's general and specific comments below.

General comments

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“It looks like the model is suitable mainly for simulating laboratory experiments, but is the model applicable for atmospheric aerosols or even simplified representations of ambient aerosols? For example, are these currently modeled alcohols and polyols common in the atmosphere, e.g., compared with abundances of organic acids? Due to their electrolytic nature organic acids are likely to partition to the water-rich phase, but are there any other common type of atmospheric organics capable of forming an organic-rich phase?”

The model framework itself allows the general computation of gas/particle partitioning including effects of a liquid-liquid phase separation. It is therefore applicable to laboratory experiments as well as the simulation of complex ambient aerosols. Due to the computational costs it is mainly suited for “offline” calculations. As outlined in Section 4.1, the six-component polyol–water–ammonium sulphate system aims at describing general gas/particle partitioning effects by the consideration of four polyols representing different volatilities and hydrophilicities. The chosen polyols may also be present to some extent in the complex mixture of ambient organics, but typically not as major compounds. However, for a general representation of the partitioning behaviour of semivolatile species, differences in the hydrophilicity and volatility properties of the model compounds are more important than the actual tropospheric abundance of the chosen species. Multifunctional organic acids, more abundant in the actual aerosol, span a range of hydrophilicities that can be represented by a mixture of different polyols. Mixtures of carboxylic acids and other organic compound classes commonly found in ambient aerosols, such as ketones, aldehydes, alcohols, sugars and multifunctional aromatic compounds, form a liquid-liquid phase separation in the presence of inorganic electrolytes at RH levels comparable to the ones computed with the six-component mixture. In the case of a liquid-liquid phase separation, rather hydrophilic compounds, such as dicarboxylic acids and polyols are found to partition significantly between the aqueous electrolyte-rich phase and the (aqueous) organic-rich phase, while less hydrophilic compounds, e.g., ketones and aromatic

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compounds, almost completely partition to the organic-rich phase. Such liquid-liquid partitioning behaviour is found in many bulk experiments for ternary and quaternary LLE of organic-water-salt systems.

Specific comments

“Due to the differences between compositions of ambient aerosol and currently modeled mixtures, do the authors think that their results can be generalized (e.g. the modified C_j^ definition)?”*

The modified C_j^* definition given in Section 3.1 is a generalization of the currently used definition ($C_j^{*,OA}$) and can be considered more applicable to aerosol mixtures where water and dissolved inorganics represent a significant fraction of the liquid phase. In case of electrolyte-free, hydrophobic organic particles, both C_j^* definitions will result in the same values and show the same RH-dependency. Therefore, we think that the results can be generalized qualitatively, regardless of the differences between ambient aerosols and the modelled mixtures.

“When comparing O : C ratios of current organics with those of the ambient aerosol (Sect. 4.3), it should be kept in mind that in the atmosphere increased O : C ratios usually mean high concentrations of organic polyacids, and their properties are different than those of the polyols.”

Organic polyacids and polyols with similar O : C (and H : C) ratios will behave differently with respect to chemical reaction mechanisms and sometimes show a different interaction-behaviour with specific inorganic ions. However, on a qualitative level and regarding the overall uncertainties in gas/particle partitioning modeling, polyacids

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and polyols with a similar carbon oxidation state can be assumed to show a similar partitioning behaviour with respect to changes in RH and electrolyte concentrations. Besides polyacids, multifunctional compounds containing several OH-groups such as levoglucosan (highly abundant in biomass burning aerosol) may also lead to an increase in the overall O : C ratio.

Technical corrections

*“Page 12498, line 12: ‘thermodynamic properties of the **phase diagram**’ maybe e.g. multicomponent mixtures?”*

We will consider the suggested correction in the revised manuscript.

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