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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.

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The authors would like to thank referee #2 for his/her review of the manuscript and valuable comments and queries. We have addressed the reviewer's comments below.

General comments

"It is not readily apparent after reading the paper how big the differences are in the activity coefficients of inorganics and organics due to non-ideal behaviour in mixtures. In other words, how much error would one introduce in say the solid-liquid equilibrium of inorganic salts in the presence of some organics by ignoring any changes in the activity coefficients in the mixture compared to their binary values. Can the authors please show 2-3 examples to illustrate the importance of organic-inorganic interactions?"

The AIOMFAC model is quite different from a simple mixing rule like the ZSR (Zdanovskii-Stokes-Robinson) approach for calculating activities. Ignoring organic-inorganic interactions in AIOMFAC for testing related effects on activity coefficients is much more complicated than it might seem to be. The way the AIOMFAC model is designed, with long-range, middle-range, and short-range contributions to activity coefficients of individual components, and with water set as the reference solvent for inorganic ions, one cannot simply set the interaction parameters between organics and ions in the middle-range part to zero, because this would not mean "ignoring" organic $\leftrightarrow$ inorganic interactions, rather, it would mean that one treats the organic main group $\leftrightarrow$ ion interactions as if they would be equal to the water $\leftrightarrow$ ion interaction. This is certainly not a good choice for most functional groups (and would not reduce the model to the binary contributions from interactions with water only). Hence, in a model like AIOMFAC organic-inorganic middle-range interaction parameters need always to be defined reasonably (by fitting them using experimental data), they cannot simply be set to zero when unknown, at least not without a risk for large deviations. However, the effects and importance of organic $\leftrightarrow$ inorganic interactions can be seen in many of the figures. Most directly in case of VLE data as shown in Fig. 2 of the article; the salt-effect isolation treatment removes the effects of organic $\leftrightarrow$ water interactions on the activity coefficients of both water and the organic compound, so that deviations of the points from the baseline ($\Delta^{sc,sf}\gamma_j^{(x)}$ = 0) in Fig. 2 (and similar

figures) represent the effect of organic ↔ ion interactions on the activity coefficients. As described by the Gibbs-Duhem relation, water ↔ ion interactions may indirectly also affect the activity coefficients of organic components. However, in AIOMFAC both interaction effects follow directly from the expressions for activity coefficients and cannot be separated in a simple manner. We will discuss this aspect in more detail in the revised manuscript. Figure 5 shows the LLE phase diagram of water + $tert$-butanol + NaCl at 298 K. Since neither the binary water + $tert$-butanol system nor the binary water + NaCl system exhibits a liquid-liquid phase separation at any mixing ratio, the phase separation in the ternary system can only be caused by interactions attributed to the salting-out effect of ions on organics. We will mention this in the revised manuscript. For LLE systems where the binary organic + water mixtures already exhibit liquid-liquid phase separation, the addition of inorganic ions usually widens the miscibility gap, an effect that can be accounted for in AIOMFAC only when organic main group ↔ ion MR interaction parameters are different from zero. Figures S0087 and S0088 from the Supplementary material to the article show activity data from binary (water-free) ethanol + $LiNO_3$ and 1-propanol + $LiNO_3$ mixtures, where in both cases the deviation from ideal behavior is obvious, especially at higher salt concentrations, requiring organic ↔ ion interactions to consider the non-ideal mixing.

"Recent experimental studies (Vaden et al., 2011; Virtanen et al., 2010) indicate that biogenic SOA is in an amorphous solid state and does not readily evaporate upon dilution. These results have challenged the traditional views of the kinetics and thermodynamics of SOA formation (gas-particle partitioning and particle phase state). Can the authors please comment if a comprehensive model such as AIOMFAC can reproduce these behaviors, or is it still quite a ways from addressing these issues."

AIOMFAC is essentially a model for the calculation of activity coefficients in liquid (bulk) mixtures assuming thermodynamic equilibrium conditions. In an absorptive

gas-particle partitioning model, AIOMFAC is responsible for the calculation of activity coefficients, which are then used in the calculation of equilibrium partial pressures of (semi)volatile species and to predict a potential liquid-liquid phase separation and its effects on the partitioning. In highly viscous or glassy systems, thermodynamic equilibrium between the components of the involved phases is not realized immediately. In contrary, equilibrium might not be reached at all or it may take very long (hours to days) to reach it. Such kinetic limitations might be included into a gas-particle partitioning model by a special parameterization but do not follow directly from a thermodynamic activity coefficient model like AIOMFAC. The issues of whether and how the kinetics and thermodynamics involved in the gas-particle partitioning of SOA in an amorphous solid or glassy state can be modeled are subjects of further research.

Specific comments

"Abstract, Line 4: Replace "room temperature" with a number (e.g., 25 C)."

In this sentence, the less strictly defined meaning of "room temperature" instead of a number like 298 K is used intentionally. Since activity coefficients are only a weak function of temperature, the variation of activity coefficients in the temperature range 298 K ±5 K is very small. Hence, using AIOMFAC for organic-inorganic mixtures in this "room temperature" range around 298 K is valid. We therefore would prefer to keep the current wording of the sentence in the abstract.

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