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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Improved AIOMFAC model parameterisation of the temperature dependence of activity coefficients for aqueous organic mixtures" *by* G. Ganbavale et al.

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The authors would like to thank Referee #2 for taking time to review our manuscript and for the positive evaluation and valuable comments. We address the Referee's comments in our response below. We will implement corresponding changes in the revised version of the manuscript.

Comments

Referee #2:

1. A more detailed discussion on the limitations and applicability of the new parameterization is needed than what is presented in section 5.3. Can the authors give more specific guidelines on what types of complex multifunctional, high molecular weight species (including oligomers) the current model can and cannot handle?
   Authors' response: It is difficult to answer this question quantitatively with regard to oligomers and other organic high molecular mass compounds. This is because our database does not contain oligomer species. Our comments on this subject are therefore mostly of qualitative character.
   The group-contribution concept does, in principal, not set any specific limit on the size or molecular mass of organic compounds. This means that oligomers can be represented with AIOMFAC or UNIFAC as long as the required functional groups are available in the model. However, this does not state anything about the accuracy of model predictions for mixtures containing such long-chain, multifunctional compounds. In our experience, AIOMFAC and UNIFAC are usually more accurate for smaller (low molecular mass) species with fewer oxygenated functional groups. The databases used to determine main group interaction parameters both for UNIFAC (for the $a_{m,n}$ parameters used in AIOMFAC) and for AIOMFAC-P3 (for the new $b_{m,n}$ and $c_{m,n}$ parameters) are clearly biased towards low-molecular mass, "monofunctional" organic compounds, since the majority of experimental data available covers these types of compounds. This is stated in Section 5.3 and we will extend the discussion on this point there. From the literature (e.g., Ninni et al., 1999) and our own experience with poly(ethylene glycol) oligomers, it is known that the standard UNIFAC parameterisation and model expressions need to be modified for aqueous oligomer/polymer solutions to achieve good model–measurement agreement. This has been done for specific types of polymers, including the introduction of specific functional groups fitted to experimental data solely of polymer systems (e.g., Ninni et al., 1999). The introduced

AIOMFAC-P3 parameterisation is for the purpose of general applicability, so that we did not introduce such changes for specific purposes. Therefore, it is expected that the AIOMFAC model may perform rather poorly when used for predicting activity coefficients in oligomer or polymer solutions. As discussed in more detail in the revised Section 5 (see our response to Referee #1), it is found that the new temperature dependence parameterisation shows particular improvement for the majority of systems containing monofunctional compounds both in the low and high temperature ranges (the temperature ranges at least 25 K above/below 298 K). For the mixtures containing multifunctional compounds present in our database (see Table 1), the improvement for the low-temperature range in comparison to AIOMFAC-P1 is more diverse: for about half of the datasets a small improvement is found while for the other half a reduced agreement is the result of the parameter optimization. Reasons for this result are discussed in (the revised) Section 5. For some systems containing multifunctional compounds, the model–measurement agreement is not good with either AIOMFAC version (e.g., for the aqueous 2-butoxyethanol system shown in Fig. 6). For such systems and corresponding main group interactions further improvement of AIOMFAC may be achieved by a refitting of certain $a_{m,n}$ parameters involved.

Manuscript revision: – Page 16936, line 10, the following sentences:

“The complexity of organics in terms of their physical and chemical properties such as size, shape and combinations of groups in multifunctional molecules are important factors that influence the quality of AIOMFAC predictions. Most of the SLE data at low temperature are limited to simple organic molecules, which thus make up the majority of the model parameterisation database. Due to this, the accuracy of AIOMFAC predictions is expected to decrease with increasing complexity of multifunctional organic compounds.”

– are replaced by the following extended discussion:

While an extensive database was compiled to allow for an improvement of the AIOMFAC model with respect to its performance at temperatures substantially

lower and higher than room temperature, there are still limitations present in both the general coverage of the extended temperature ranges by experimental data. The complexity of organic molecules in terms of their physical and chemical properties such as size, shape and combinations of functional groups, particularly the number and proximity of oxygen-bearing functionalities, are important factors that influence the quality of AIOMFAC predictions. Of interest for atmospheric aerosol systems are datasets containing multifunctional organic compounds, such as sugar-like compounds, di- and polycarboxylic acids, hydroxylated ketones and functionalized aromatic compounds. We have added many experimental thermodynamic equilibrium datasets that cover systems containing such compounds (e.g., sorbitol, 1,2,7,8-octanetetrol, sucrose, raffinose, citric acid, malonic acid, 2-isopropoxyethanol, vanillylmandelic acid, etc.; see Table 1 for a complete list), yet overall the database remains dominated by small, monofunctional organic compounds. This possibly limits the accuracy of AIOMFAC-P3 for predicting activity coefficients in multicomponent systems containing multifunctional, high-molecular mass species. This is a disadvantage not just for AIOMFAC-P3 or this work, but generally rooted in the very limited amount of experimental data covering such systems (especially at temperatures much lower/higher than 298 K). Due to this, the accuracy of AIOMFAC predictions is expected to decrease with increasing complexity of organic compounds.

As discussed in more detail at the beginning of Section 5, it is found that the new temperature dependence parameterisation shows particular improvement for the majority of systems containing monofunctional compounds both in the low and high temperature ranges (the temperature ranges at least 25 K above/below 298 K). In case of the mixtures containing multifunctional compounds present in our database, the improvement for the low-temperature range in comparison to AIOMFAC-P1 is more diverse: for about half of the datasets a small improvement is found while for the other half a reduced agreement is the result of the parameter optimization. For some systems containing multifunctional compounds, the model–measurement agreement is not good with either AIOMFAC version (e.g., in case of the aqueous 2-butoxyethanol system shown in Fig. 6). For such systems and corresponding main group interactions, further improvement of AIOMFAC may only be achieved by a refitting of certain $a_{m,n}$ interaction parameters involved. It is known that the standard UNIFAC parameterisation and model expressions need to be modified for aqueous oligomer/polymer solutions to achieve good model–measurement agreement (e.g., Ninni et al., 1999). This has been done in previous work targeting specific types of polymers, including the introduction of specific UNIFAC groups fitted to experimental data exclusively of such polymer systems (e.g., Ninni et al., 1999). The introduced AIOMFAC-P3 parameterisation has as purpose general applicability, as is the case for AIOMFAC-P1. Therefore, it is expected that the AIOMFAC model may perform rather poorly when used for predicting activity coefficients in oligomer/polymer solutions. For such systems, the application of specifically fitted models is recommended.

2. The authors mention in the introduction "Thermodynamic phase equilibrium calculations allow to determine whether the aerosol phase is a liquid (or viscous amorphous phase), a crystalline solid, or a mixture of solid and liquid phases and to what degree semivolatile species partition to the condensed phases." The question is can AIOMFAC actually predict or distinguish between liquid and viscous (semisolid) amorphous phases? If so, how is viscosity and temperature dependence of viscosity predicted (or taken into account)? A discussion on these points should also be included in section 5.3.
   Authors' response: The wording in the article was potentially misleading. This has been revised (see also the related response to Referee #1, comment 2). The point is that with respect to a thermodynamic equilibrium calculation, it does not matter whether a homogeneous (amorphous) phase is a low-viscosity

liquid or a high-viscosity "viscous amorphous" phase, as long as it is well mixed, i.e. homogeneous, at equilibrium. It is not about predicting the viscosity of the solution.
   Manuscript revision: – Page 16909, line 23, the sentence was revised to:
   Thermodynamic phase equilibrium calculations allow to determine whether the aerosol phase is a liquid (here liquid also refers to a homogeneous, yet potentially highly viscous amorphous phase), a crystalline solid, or a mixture of solid and liquid phases (when assumption of equilibrium is appropriate) and to what degree semivolatile species partition to the condensed phases (Pankow, 2003; Zuend et al., 2010; Zuend and Seinfeld, 2012; Shiraiwa et al., 2013).

3. Finally, these limitations of the model should be briefly mentioned in the abstract and the conclusions section.
   Authors' response: We briefly mention the limitations regarding multifunctional compounds and oligomers in the abstract and conclusions section of the revised manuscript.
   Manuscript revision: – Abstract, Page 16908, line 26, the last sentence is revised to:
   The new parameterisation of AIOMFAC agrees well with a large number of experimental datasets. Larger model–measurement discrepancies were found particularly for some of the systems containing multifunctional organic compounds. The affected systems were typically also poorly represented at room temperature and further improvements will be necessary to achieve better performance of AIOMFAC in these cases (assuming the experimental data are reliable). The performance of the AIOMFAC parameterisation is typically better for systems containing relatively small organic compounds and larger deviations may occur in mixtures when molecules of high structural complexity such as highly oxygenated compounds or molecules of high molecular mass (e.g.,

oligomers) prevail. Nevertheless, the new parameterisation enables the calculation of activity coefficients for a wide variety of different aqueous/water-free organic solutions down to the low temperatures present in the upper troposphere.

– Conclusions, Page 16937, line 10, the following statements are added:
In addition, larger discrepancies in model–measurement agreement were found in particular for some of the systems containing multifunctional organic compounds. The affected systems were typically also poorly represented at room temperature. Further investigations will be needed to thoroughly address these issues and achieve better performance of AIOMFAC in such cases over the full temperature range of interest. The performance of the AIOMFAC parameterisation is typically better for systems containing relatively small organic compounds and substantial deviations may occur in mixtures when molecules of high structural complexity such as highly oxygenated compounds or molecules of high molecular mass (e.g., oligomers and polymers) prevail.

References

- Ninni, L., Camargo, M. S., and Meirelles, A. J. A.: Water activity in poly(ethylene glycol) aqueous solutions, Thermochimica Acta, 328, 169-176, 1999.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 16907, 2014.