Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-1084-RC1, 2020


Atmospheric Chemistry and Physics Discussions

# *Interactive comment on* "Thermodynamic properties of isoprene and monoterpene derivedorganosulfates estimated with COSMO*therm*" *by* Noora Hyttinen et al.

**Anonymous Referee #1**

Received and published: 20 January 2020

General Comments:

Isoprene and monoterpene organosulfates contribute significantly to atmospheric secondary aerosol formation. However, their physical chemical properties are rarely studied, due to the difficulty in isolating adequate quantity of individual chemicals and challenge in the measurement. In this paper, the authors used computation method COSMOtherm to predict thermodynamic properties for organofulfates, including solubilities, activities and saturation vapor pressures, pKa, salting out effect. The authors provide adequate information on the technical details. A major comment is that the authors should add discussion about the uncertainties of the predicted values for dif-



ferent properties. This could be either from literature that have used COSMOtherm to predict different physical-chemical properties (e.g. Henry's law constants, solubility, pKa, salting out effect, saturation vapor pressure, etc.) or from the own estimation.

Specific comments:

Line 67, the authors may consider describing COSMOtherm more here, since majority of the readers of this paper are not familiar with the program.

Line 104, in reality, OS likely have conformers with intramolecular hydrogen bonds, what is the uncertainty if the intramolecular hydrogen bonding is not considered (or only include conformers containing no intramolecular hydrogen bonds) in the calculation? In addition, is the version of COSMOtherm program used by Kurten et al. (2018) the same as in this paper, if not, are there any improvement with intramolecular hydrogen bond representation in the updated version of COSMOtherm?

Section 3.2, it was mentioned early that organosulfates dissociate significantly in pure water, did the authors consider dissociation of organosulfates when calculating solubility in ammonium sulfate or bisulfate solutions?

Line 206, it seems that the authors used hydrated sodium cations for the description of sodium cation solvation for organosulfate sodium salts. Did they use hydrated salt ions for ammonium sulfate and ammonium bisulfate? If not, why?

Line 263 and others, the authors mentioned 0.09 mole fraction salt solution in multiple places in the paper. Why is 0.09 mole fraction used? Is this the saturation concentration of a salt in water?

Line 413, Figure 4 and 9 show the influence of ammonium sulfate and ammonium bisulfate on solubility and Henry's law constants for different species. I understand that there are no experimental data available to validate the predicted values for the species of interest. However, the authors should do calculations for chemicals with experimental data available to validate the model prediction. Especially, since the previous publica-

tions (Endo et al. 2012, Wang et al., 2014, Toivola et al., 2017) on the topic of using COSMOtherm to predict salt out effect observe an overestimation of salting out effect with COSMOtherm in comparison to experimental values.

Endo, S., Pfennigsdorff, A., Goss, K-U. Salting-out effect in aqueous NaCl solutions: trends with size and polarity of solute molecules. Environ. Sci. Technol., 2012, 46, 3 1496-1503.

Wang, C., Lei, Y. D., Endo, S., Wania, F. Measuring and modeling the salting-out effect in ammonium sulfate solutions, Environ. Sci. Technol., 2014, 48, 13 238-13 245.

Toivola, M., Prisle, N. L., Elm, J., Waxman, E. M., Volkamer, R., and Kurtén, T.: Can COSMOTherm Predict a Salting in Effect? J. Phys.Chem. A, 2017, 121, 6288–6295.

The authors predicted the Henry's law constant for organosulfates in water. However, in the atmosphere there are also large volume of organic phase available. What about the Henry's law constant into organic phase?

---

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-1084, 2019.