Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-1084-RC2, 2020

Atmospheric Chemistry and Physics
Discussions
Open Access

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

Anonymous Referee #2

Received and published: 13 February 2020

In this work, the authors have used the COSMOtherm program to calculate both properties of atmospherically relevant monoterpene and isoprene derived organosulfates (such as solubilities, activities and saturation vapor pressures). The new modeled results are important for us to better understand the atmospheric impacts and fates of organosulfates. The model simulations are carefully designed and run with strong justifications and assumptions. The paper is well written and is suitable for publication in ACP. I have two major suggestions:

1. It is understood that there are uncertainties for the model simulations. The authors have done a very nice work in explaining your model simulations. However, it would

be still useful for the readers to know what would be the potential uncertainties of the modeled results (e.g. what is the possible range of the model results instead of a single value?).

2. To date, it remains unclear how the sulfate group would affect the properties of the organic compounds. It would be useful if the authors could discuss how the presence or absence of sulfate group would change the properties of an organic molecules based on their model simulations.

Minor comments:

Abstract, “The estimated pKa values of all the organosulfates indicate a high degree of dissociation in water, leading in turn to high dissociation corrected solubilities.” Any explanation from the model simulations?

Line 45, “The hygroscopic properties of organosulfate containing aerosol have been measured using sodium salts of alkane sulfates (Woods III et al., 2007; Estillore et al., 2016) and limonene derived organosulfates (Hansen et al., 2015). Limonene derived organosulfate was demonstrated to lower the surface tension of aqueous solutions even more effectively than atmospherically relevant strong organic acids (Hansen et al., 2015).” Could the authors compare their model results with some of these literature data?

Line 47, “In addition, Nguyen et al. (2014a, b) have seen indications of long-range transport of organosulfates, suggesting that organosulfates must have sufficiently low volatilities to remain in the aerosol-phase over a wide range of atmospheric conditions.” This observation does not consistent with the model results? As stated in the abstract, “Based on the estimated saturation vapor pressures, the organosulfates of this study can all be categorized as semi- or low-volatile, with saturation vapor pressures 4 to 8 orders of magnitude lower than that of sulfuric acid” . Do these modelled results support by the laboratory and field observations?

Line 80, “The non-systematic conformer generation in COSMOconf has been shown to lead to significantly different results in COSMOtherm depending on the initial geometry with molecules containing hydroxy and hydroperoxy functional groups (Kurtén et al., 2018). Based on the recommendation by Kurtén et al. (2018), we therefore used the systematic conformer sampling with the MMFF force fields in the Spartan ’14 program (Wavefunction Inc., 2014).” While the organosulfates contain a sulfate group, would the recommendation made by Kurtén et al. (2018) be the best option for the organosulfates investigated in this work? More elaboration would be needed.

Line 96, “All calculations were done at 298.15 K and we assume that all of the organosulfates (OS) and the isoprene epoxydiols (IEPOX) are liquids.” Please elaborate why we could assume all organosulfates investigated in the work are liquids in their pure forms at 298K.

Line 104, “Kurtén et al. (2018) found that COSMOtherm overestimates the effect of intramolecular hydrogen bonds and recommended that only conformers containing no intramolecular hydrogen bonds should be used in saturation vapor pressure calculations. We therefore omitted all conformers containing intramolecular hydrogen bonds from the calculations of OS and IEPOX.” This argument is okay. However, how this assumption would affect the model results?

Line 268, “Compared to the binary LLE solubility, the solubility calculated as a relative solubility for monoterpene derived organosulfates is on average 3.1 times higher (1.8-5.5) using (NH4)2SO4 solutions as reference, and 2.2 times higher (1.7-2.9) using NH4HSO4 solutions.” Could the authors elaborate why the relative solubility for monoterpene derived organosulfates is higher than ammonium sulfate and ammonium bisulfate?

Line 286, “The organosulfates are therefore estimated to be of equivalent strength or even stronger acids than H2SO4, and thus for all practical purposes fully dissociate in near-neutral solutions and even solutions at most atmospherically relevant pH.” These

are important results. Any literature data to support these findings?

Line 288, “For all organic compounds, dissociation corrected solubilities correspond to mole fractions higher than 1. This unphysical result is likely caused by inability to accurately capture solution behavior of very strongly acidic compounds.” How would this factor affect other modelled results?

Line 326, “With O:C ratios of the monoterpene and isoprene derived organosulfates in the ranges 0.5–0.7 and 1.2–1.4, respectively, these results are consistent with the present work. On the other hand, in experiments of OH oxidized α-pinene and water system (Ham et al., 2019) only a single organic-rich phase was observed, whereas LLPS was seen between water and ozone oxidized α-pinene products (Ham et al., 2019) or OH oxidized isoprene products (Rastak et al., 2017).” For organosulfates, 4 oxygen atoms are associated from the sulfate group. Would this affect how we interpret the O:C ratio?

Line 375, “We calculated saturation vapor pressures for the neutral organic compounds at 298.15 K (Table 1). Comparing the studied organosulfate compounds based on their functional groups, those containing carboxylic acid groups, i.e., α-pinene-OS-5 and α-pinene-OS-6, have the lowest saturation vapor pressures.” How the presence of sulfate group would affect the saturation vapor pressure of the organic compounds?

Line 403, “Among the studied organics, Henry’s law solubility is the highest for monoterpene and isoprene derived organosulfates containing the highest number of oxygen atoms and the lowest for methyl bisulfate and the IEPOX isomers.” Also, how the presence of sulfate group would affect the Henry’s law solubility of the organic compounds?

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