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Influence of non-ideality on condensation to aerosol

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Abstract. Secondary organic aerosol (SOA) is a complex mixture of water and organic molecules. Its composition is determined by the presence of semi-volatile or non-volatile compounds, their saturation vapor pressure and activity coefficient. The activity coefficient is a non-ideality effect and is a complex function of SOA composition. In a previous publication, the detailed chemical mechanism (DCM) for α-pinene oxidation and subsequent aerosol formation BOREAM was presented. In this work, we investigate with this DCM the impact of non-ideality by simulating smog chamber experiments for α-pinene degradation and aerosol formation and taking the activity coefficient into account of all molecules in the aerosol phase. Several versions of the UNIFAC method are tested for this purpose, and missing parameters for e.g. hydroperoxides and nitrates are inferred from fittings to activity coefficient data generated using the SPARC model. Alternative approaches to deal with these missing parameters are also tested, as well as an activity coefficient calculation method based on Hansen solubility parameters (HSP). It turns out that for most experiments, non-ideality has only a limited impact on the interaction between the organic molecules, and therefore on SOA yields and composition, when water uptake is ignored. The reason is that often, the activity coefficient is on average close to 1 and, specifically for high-VOC experiments, partitioning is not very sensitive on the activity coefficient because the equilibrium is shifted strongly towards condensation. Still, for ozonolysis experiments with low amounts of volatile organic carbon (low-VOC), the UNIFAC parameterization of Raatikainen et al. leads to significantly higher SOA yields (by up to a factor 1.6) compared to the ideal case and to other parameterizations. Water uptake is model dependent, in the order: ideal > UNIFAC-Raatikainen > UNIFAC-Peng > UNIFAC-Hansen ≈ UNIFAC-Magnussen ≈ UNIFAC-Ming. In the absence of salt dissolution, phase splitting from pure SOA is unlikely.

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