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Atmospheric Chemistry and Physics
Discussions

Interactive comment on “Effects of Liquid–Liquid Phase Separation and Relative Humidity on the Heterogeneous OH Oxidation of Inorganic–Organic Aerosols: Insights from Methylglutaric Acid/Ammonium Sulfate Particles” *by* Hoi Ki Lam et al.

Anonymous Referee #1

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Here follows the review of the manuscript entitled “Effects of Liquid–Liquid Phase Separation and Relative Humidity on the Heterogeneous OH Oxidation of Inorganic-Organic Aerosols: Insights from Methylglutaric Acid/Ammonium Sulfate Particles” by Lam et al. In this laboratory work the authors study how the OH heterogenous reactivity changes as inorganic/organic particles composed of ammonium sulfate (AS) and 3-methyglutaric acid (MGA) undergo liquid-liquid phase separation (LLPS) in response to humidity changes. This work is, in part, based on the previously applied experimental procedures by Xu et al. (ACP, 2020). Particles with an organic-to-inorganic dry mass ratio (OIR) of 1 experience LLPS at about 75% RH displaying core-shell or partially engulfed morphology. The authors observe that OH reactivity is higher for the LLPS state compared to the purely liquid phase state. Application of phase separation measurements and model simulations suggest that the enhanced reactivity is due to the higher concentration of MGA at the droplet surface which in turn increases the reactive collision probability between MGA and OH. Model simulations of the diffusion of MGA, including the core-shell configuration, provide reasoning that the diffusivity of MGA is sufficiently fast that reactivity is not diffusion limited. Therefore, the authors conclude that MGA surface concentration is likely the determining factor of the overall observed OH reactivity.

The topic of this study fits very well within the scope of Atmospheric Chemistry and Physics. I enjoyed reading this manuscript. The experimental approach and methods appear to be sound and present a continuation and extension of a previously published study by this group. This work adds significantly to our understanding of how particle phase changes impact gas-to-particle interactions, specifically the chemical oxidation of organic particular matter. I only suggest minor revisions.

For the molecular dynamics simulations, it would be nice to set those results in context to previous work. Do the general results/trends observed here agree with previous studies? For example, the work by Tobias and Jungwirth groups examining the distribution of ions in the aqueous phase. One would assume SO42- being more in the bulk than NH4+. However, in the presence of an organic surfactant this may change. Some discussion referring to previous MD studies on aqueous solutions and presence of surfactants should be added.

As stated AIOMFAC-LLE (VISC) is a group-contribution model and not specifically setup to simulate the organic–inorganic system studied here. However, when looking at the results displayed in Fig. 4, is there a way to give the range of uncertainties in shown values derived by this model? I assume the model is fit to observational data of single component data sets, etc. What would be the expected value ranges for the binodal limits, water activity, etc.? This may not be easy to answer but a best-guess of value ranges would be appreciated. Also, I believe "LLE" is not spelled out.

Line 58: The study by Slade et al. (2015) and (2017) could be added here which relate OH uptake with particle hygroscopicity of amorphous organic and inorganic/organic particles.

Line 61: The authors might add the recent study by Li et al. (2020) on OH uptake by organic matter in various phase states.

Line 72-78: Potentially relevant to this study: Charnawskas et al. (2017) documented core-shell morphology of submicron inorganic/organic particles using X-ray microscopy (similar to this study, i.e., core-shell).

Line 292: I feel this sentence is missing a word. The single liquid phase has an order of magnitude. . .greater than what? Maybe I misunderstand this sentence.

Line 450: What are the potential uncertainties in AIOMFAC-VISC and thus the uncertainties in the time scale for diffusive mixing? Since the values are close to the time of collision events, it may be good to have a boundary on those theoretically derived values.

Line 486: See my comments above on MD studies.

Line 552-555: The study by Li et al. (2020) may be relevant for this statement.

Technical correction:

Line 373: I suggest to omit "occurred".

References:

Slade, J. H., Thalman, R., Wang, J., and Knopf, D. A.: Chemical aging of single and multicomponent biomass burning aerosol surrogate particles by OH: implications

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