Anonymous Referee #1

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.

We would like to sincerely thank the reviewer for his/her thoughtful comments and suggestions. Please see our responses to reviewer's comments and suggestions below.

Reviewer's Comment #1
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 SO_4^{2-} being more in the bulk than NH_4^+. 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.

Authors' Response
We would like to thank the reviewer for suggesting a comparison with the previous results. We put the density profiles of our SO_4^{2-} and NH_4^+ models in Figures S11 (slabs) and S12 (droplets) in the supplement information. Our models are consistent with the previous study by Gopalakrishnan et al. (2005) that shows NH_4^+ prefers the interface more so than SO_4^{2-}. In our study, the presence of 3-MGA does not change this trend. 3-MGA may have pushed the maximum densities of NH_4^+ and SO_4^{2-} slightly more towards the bulk when compared to the previous study, but the differences in the system sizes and simulation parameters may have played a role.

We have now added the following the main text in the revised manuscript.
Line 499, "In a previous study, Gopalakrishnan et al. (2005) carried out polarizable MD simulations to study the propensity of NH_4^+ and SO_4^{2-} for the air–liquid interface. They showed that NH_4^+ ions have a stronger preference for the interface than SO_4^{2-}. With the addition of 3-MGA near the water interface in our MD simulations, we have observed similar results (see Figures S11 and S12 in the supplemental information), namely that NH_4^+ prefers proximity to the interface more so than SO_4^{2-}. The presence of 3-MGA may have pushed the maximum densities of NH_4^+ and SO_4^{2-} slightly more towards the bulk relative to the interface, but such differences may have been due to the differences in system sizes and other simulation parameters."

Reference
Gopalakrishnan, S.; Jungwirth, P.; Tobias, D. J.; Allen, H. C. Air−Liquid Interfaces of Aqueous Solutions Containing Ammonium and Sulfate: Spectroscopic and Molecular Dynamics Studies. J. Phys. Chem. B, 109, 8861–8872, 2005.

Reviewer's Comment #2
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.

Authors' Response
Thanks for the comment. This question and our answer refer to Figure 4 and associated text in Sect. 3.2. The reviewer is correct in stating that providing a range of uncertainties for the binodal limit curve of the liquid–liquid equilibrium (LLE) prediction is not easy, as will be explained in the following. Absent reliable quantitative measurements of the binodal curve for this system, we can only provide estimates supported by limited evidence. We will also spell out the abbreviations LLE and AIOMFAC in the revised manuscript.

The predicted phase diagram shown in Figure 4 for the ternary aqueous 3-MGA/AS system with OIR = 1 has been computed by using the previously determined parameter set of the AIOMFAC group-contribution model from the work by Zuend et al. (2011). A specific dataset of this ternary system was not directly involved in the optimization of the AIOMFAC model parameters and, hence, the model is not expected to perform optimally for this system. However, the training and optimization of the AIOMFAC model by Zuend et al. (2011) involved one multicomponent data set of three dicarboxylic acids with 6 carbon atoms, including 3-methylglutaric acid, as well as ammonium sulfate (Fig. S0220 from the supplementary information document of Zuend et al. 2011; reproduced below for reference). That system is expected to behave similarly to the ternary 3-MGA/AS system from our current study, although the involved OIR differ.

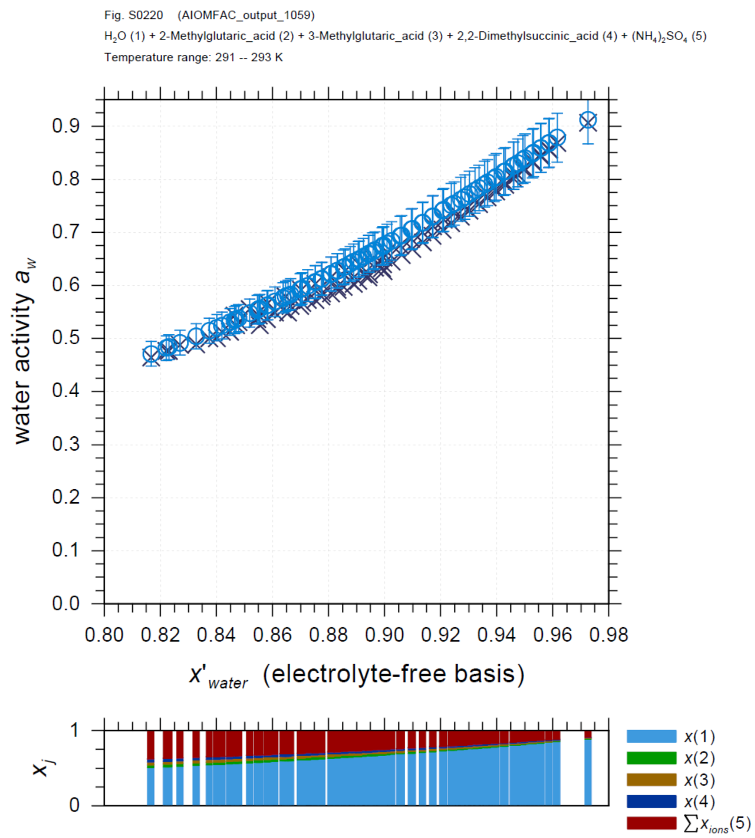

Fig. S0220 reproduced from Zuend et al. (2011); shown in their supplementary information. Model–measurement comparison for the system water (1) + 2-Methylglutaric acid (2) + 3-Methylglutaric acid (3) + 2,2-Dimethylsuccinic acid (4) + ammonium sulfate (5) at temperatures near 293 K. The mixing ratio among the organic diacids is 1:1:1 by mass. Composition is given in mole fractions (x). Cross symbols mark water activity measurements by an electrodynamic balance or a water activity meter at higher a_w, open circles and error bars are the model predictions by AIOMFAC pertaining to each composition point. The error bars indicate cumulative AIOMFAC prediction sensitivity to a composition uncertainty of 0.01 in mole fraction; see details in Zuend et al. (2011).

Fig. S0220 indicates that measured and predicted water activities are approximately in agreement when accounting for a mole fraction composition uncertainty of about 0.01, which can lead to larger uncertainty in predicted water activity (error bars in the attached figure) of approximately ±5 % at water activities above ~0.6. Collectively, the model predictions also show a slight high bias in predicted water activity compared to the measurements, which may explain at least partially why the onset of liquid–liquid phase separation predicted by AIOMFAC-LLE in Figure 4 for OIR = 1 is at a higher water activity of about 0.83 than the one determined by the microscopy experiments (a_w ~0.75).

Therefore, we estimate that the onset RH of LLPS is predicted with a potential high bias of about 5–8%. From this work and previous comparisons, e.g. Song et al. (2012a) it seems to be the case that for systems involving dicarboxylic acids and ammonium sulfate AIOMFAC tends to predict a higher onset RH of LLPS than is usually determined from droplet or bulk measurements. This is mentioned in Sect. 3.2, lines 271–274 in the original manuscript. Estimating the error in the extent (or area) of phase separation indicated by the “width” of the area enclosed by the binodal curve in Figure 4 in terms of the mass fraction of salt on water-free basis, is difficult. Given that the Gibbs energy difference between a single mixed phase and LLPS is relatively small in the composition space near the binodal limit (and between binodal and spinodal curves), uncertainties in the predicted activity coefficients of the mixture components can amplify. To provide a rough estimate, we would also expect about 0.1 units of dry mass fraction uncertainty in w_d(salt). The location of the critical point (where binodal and spinodal curves touch) is expected to remain in the range of w_d(salt) = 0.4 to 0.5.

We have made the following changes to the manuscript.

We rephrase the sentence to define abbreviations. Line 262: "Thermodynamic phase equilibrium calculations were also performed using the Aerosol Inorganic–Organic Mixtures Functional groups Activity Coefficients (AIOMFAC) liquid–liquid equilibrium (LLE) model, hereafter referred to as AIOMFAC-LLE model, to compare the results of the experimentally observed LLPS range and onset mechanism (Zuend et al., 2008, 2010, 2011; Zuend and Seinfeld, 2013)."

Line 276: we add "Based on this comparison and other related comparisons of AIOMFAC-LLE predictions with measurements (Song et al., 2012a), we estimate that the onset of LLPS is predicted within about 10 % uncertainty in RH."

Reviewer's Comment #3
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.

Authors' Response
We have added these two references.

Reviewer's Comment #4
Line 61: The authors might add the recent study by Li et al. (2020) on OH uptake by organic matter in various phase states.

Authors' Response
We have added this reference.

Reviewer's Comment #5
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).

Authors' Response
We have added this reference.

Reviewer's Comment #6
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.

Authors' Response

Thanks for the comment. In the original manuscript, we intended to mention that the viscosity of an aqueous 3-MGA/AS droplet with a single liquid phase ranges from ~10^{-3} Pa s to 10^{-2} Pa s. We have revised the sentence in the revised manuscript.

Line 296, "As shown in Figure S3, when the RH > SRH, the viscosity of an aqueous 3-MGA/AS droplet with a single liquid phase ranges from ~10^{-3} to 10^{-2} Pa s and increases with decreasing RH."

Reviewer's Comment #7

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.

Authors' Response

The uncertainty in predicted viscosities of the organic-rich phase is indicated in Fig. S3 by the red shaded area. These uncertainty estimates were generated using AIOMFAC-VISC by accounting for a ± 5 % uncertainty in the estimated glass transition temperatures of the pure components. Here, the uncertainties are about -0.21 to +0.34 in $\log_{10}$[viscosity / (Pa s)] units for the RH range from 55 % to 70 %. To provide additional data on viscosity, diffusivity and mixing timescale estimates, we have added additional data in Table S1 for these properties of the organic-rich phase. Aside from the already listed best estimates, we list now also the estimated lower and upper bounds for these predicted parameters. For example, the uncertainty in the predicted phase viscosity translates to estimated bounds on the mixing timescale of 3.6 to 13.8 μs at 60 % RH; with a best estimate of 6.6 μs.

We list now also predicted lower and upper bounds for values related to the viscosity predictions in Table S1.

Excerpt of revised Table S1 showing organic-rich phase viscosities (AIOMFAC-VISC estimate) at 293 K and associated diffusion coefficients and mixing times. Lower and upper value estimates for phase viscosities and derived diffusivity values are listed in brackets (based on 5 % uncertainty in pure-component glass transition temperature).

RH (%)	**55**	**60**	**65**	**70**	**75**	**80**	**85**	**88**
Viscosity of the organic-rich phase (Pa s)	0.0958 [0.051; 0.21]	0.0636 [0.035; 0.133]	0.0421 [0.024; 0.083]	0.0275 [0.016; 0.051]	/	/	/	/
Diffusion coefficient of 3-MGA molecules in organic-rich phase (× 10^{-12} m^2 s^{-1})	6.15 [11.6; 2.79]	9.26 [16.8; 4.43]	14.0 [24.2; 7.09]	21.4 [35.3; 11.5]	/	/	/	/
Diffusive mixing time of organic-rich phase (μs)	10.2 [5.4; 22.5]	6.6 [3.6; 13.8]	4.2 [2.4; 8.4]	2.6 [1.6; 4.9]	/	/	/	/

Reviewer's Comment #8

Line 486: See my comments above on MD studies.

Authors' Response

Please kindly see our response to Reviewer 1's Comment #2.

Reviewer's Comment #9
Line 552-555: The study by Li et al. (2020) may be relevant for this statement.

Authors' Response
We have added this reference.

Reviewer's Comment #10
Technical correction: Line 373: I suggest to omit "occurred".

Authors' Response
We have made the correction.

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 for cloud condensation nucleus activity, Atmos. Chem. Phys., 15, 10183–10201, 2015.

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Li, J., Forrester, S. M., and Knopf, D. A.: Heterogeneous oxidation of amorphous or- ganic aerosol surrogates by O_3, NO_3, and OH at typical tropospheric temperatures, At- mos. Chem. Phys., 20, 6055–6080, 2020.

Charnawskas, J. C., Alpert, P. A., Lambe, A. T., Berkemeier, T., O'Brien, R. E., Mas- soli, P., Onasch, T. B., Shiraiwa, M., Moffet, R. C., Gilles, M. K., Davidovits, P., Worsnop, D. R., and Knopf, D. A.: Condensed-phase biogenic-anthropogenic inter- actions with implications for cold cloud formation, Faraday Discuss., 200, 165–194, 2017.