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## Comment on acp-2021-836

Anonymous Referee #1

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Referee comment on "A predictive viscosity model for aqueous electrolytes and mixed organic–inorganic aerosol phases" by Joseph Lilek and Andreas Zuend, Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-836-RC1>, 2021

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This paper describes an extension of the AIOMFAC-VISC model, which previously could only be used to predict the viscosity of organic aerosol. This work focuses on the development of an electrolyte viscosity predictive model and its integration with the previous version of the model for organics, allowing for predictions on mixed inorganic-organic aerosol systems.

AIOMFAC is one of the most commonly used models to predict activity coefficients and composition of organic and/or inorganic aerosols at variable temperature and RH. The added capability of predicting the viscosity of electrolytes and organic/inorganic mixtures provided with this work is of great importance for the aerosol research community and it is unique in its kind and scope.

General comments:

Overall, the manuscript is well written and understandable by readers that do not necessarily know the specifics of the thermodynamic modelling of aerosols. The authors make substantial effort to explain and justify all the decisions they made in the development of their modelling approach. Comparison of results from the fitted model for ternary/quaternary inorganic mixtures and for mixed organic/inorganic systems provides indication that the model performs well on increasingly complex systems.

I think there are two (significant but not major) points that should be addressed by the authors, which are detailed in my specific comments below. Briefly, the first one is about the 'unphysical' predictions of the viscosity for binary solutions of electrolytes that either crystallize or form gels. The authors should make more explicit why they decided to leave these 'unphysical' predictions in their model (which I believe is to be able to provide simulations for more complex inorganic/organic mixtures), rather than for example

preventing the model to provide predictions where the formation of gels or crystalline solids is expected. Secondly, considering the limited data availability used to constrain the model and given the knowledge that the authors have gained on what are the most significant factors that influence their model's predictions, I think the authors should consider providing more specific suggestions on what further measurements of viscosity are needed to incrementally better constrain the predictions of their model.

Below I am providing specific comments on the manuscript, most of which are simple requests of clarification. I recommend publication of this high-quality and high-impact paper after the authors address my (mostly minor) comments.

Specific comments:

Page 3, line 80. It does seem a little odd to the reader that AIOMFAC-VISC is introduced before the broader framework of AIOMFAC in this paragraph. I would also argue that the positioning of section 1.3 between the two sections with titles "Two popular frameworks: Jones–Dole and Eyring" (1.2) and "Applying Eyring's basis for aqueous electrolyte viscosity in AIOMFAC-VISC" (2.1) is somewhat breaking the flow of this part of the manuscript. The authors should consider introducing AIOMFAC first, then AIOMFAC-VISC, then discuss the two possible approaches, why they chose Eyring's and finally how it's implemented in AIOMFAC-VISC.

Page 5, line 134: "AIOMFAC defines ion molality as moles of dissociated ion per 1 kg of solvent mixture (water + organics) as opposed to per 135 1 kg of water, and this must be taken into account when organics are present." Can the authors briefly explain the reason for this and/or reference a previous paper where this aspect is described?

Page 10, line 240: "More recently, techniques such as poke-and-flow, bead mobility, and holographic optical tweezers 250 have enabled viscosity measurements for droplets (Reid et al., 2018). Due to their small size and absence of contact with solid surfaces, aqueous droplets often attain concentrations of solute exceeding the bulk solubility limits, suggesting higher viscosities are likely to occur in nature." The authors seem to suggest that with these recently developed techniques more data should become available in the future to cover more concentrated solutions. If that is the case, it should be made explicit, otherwise this sentence about experimental techniques is lacking some context as is.

Page 20, line 493: "Two systems stand out, however:  $\text{NaNO}_3$  and  $\text{Ca}(\text{NO}_3)_2$ , both of which show positive bias. These two systems include some of the highest viscosity values among the available measurements, which is a factor in their large contributions to the overall objective function error.  $\text{NaNO}_3$  and  $\text{Ca}(\text{NO}_3)_2$  also include both bulk and droplet-based measurements, and these data do not agree at low water content, leading to larger fit residuals for these systems.". Please provide quantitative ranges on what are "some of the highest viscosity values among the available measurements". In addition, I would suggest to mention here that data for these systems are shown later in figure 8, in case

the reader was wondering what those look like when reading this paragraph.

Page 24, Figure 3a: Can the authors explain why both the two bottom panels with information on the chemical composition and the predicted viscosity trends have a stepwise trend and are not smooth?

Page 24, line 526: "Considering the much larger viscosity scale that is typical for atmospheric aerosol cases, this level of agreement with the measurements is very encouraging." It's unclear to me what the authors mean with this statement. Considering that the data in figure 3a is in the mPa range, and aerosols in semisolid or solid states can have a viscosity of several orders of magnitude higher, why are the authors saying that agreement at low viscosity is encouraging for higher viscosity cases? This needs to be clarified.

Page 25, line 537: "In each of those multi-ion cases involving chloride, bromide, nitrate, sulfate, or any combination of these as anions, AIOMFAC-VISC performs as well or better than the Laliberté model. Given that those data sets were used in the overall fit of the AIOMFAC-VISC parameters, this is not unexpected." Have the authors performed any sensitivity test to evaluate what the performance on these ternary and the quaternary systems is when they are not included in the model training set? It would be interesting to see how well a model fitted only on binary mixtures would perform on the prediction on ternary/quaternary solutions. Considering that the authors seem to suggest that more measurements are needed to better constrain AIOMFAC-VISC, such sensitivity test could provide important information about what are the real priorities in terms of what additional measurements are really needed. In other words, what is more important to improve the performance of the model, further measurements on binary mixtures (with different electrolytes, covering larger concentration ranges, etc.) or more data on different ternary/quaternary systems? In the conclusion the authors state: "Future experimental work on a wider range of compositions and a more diverse set of multicomponent systems (presently highly data-limited) may provide data and insights that could allow further refinements of the organic-inorganic mixing model". I am wondering if this statement could be expanded if the authors have more specific ideas on the possible priorities I have discussed above.

Page 29, line 571: "Due to the lack of viscosity measurements at low mass fraction of water and the tendency for salts to crystallize at high concentration, it is difficult to determine quantitatively which model/curve, if any, is correct for any given case. What is clear, however, is that AIOMFAC-VISC provides an excellent level of accuracy in the composition range where measurement data are available and can be used in place of the Laliberté model in most instances". In most of the cases in figures 4-7, AIOMFAC-VISC predicts a higher viscosity at low mass fraction of water. Do the authors have hypotheses about why that is the case? It would be interesting if they could comment on this aspect in the manuscript and share possible explanations of this observation.

Page 30, Figure 8: Power et al. (Power, R. M., Simpson, S. H., Reid, J. P. & Hudson, A. J. The transition from liquid to solid-like behaviour in ultrahigh viscosity aerosol particles.

*Chem. Sci.* **4**, 2597–2604 (2013)) have measured the viscosity of binary NaCl solutions down to  $a_w=0.7$  (which corresponds to about a mass fraction of water of 0.7, according to a quick check from the E-AIM model). Have the authors considered this dataset in their work? Considering how limited the data from aerosol droplets measurements is, would it be worth to include this dataset too? I am not sure if it would be necessary to refit the model to include it, but it might be good to at least add a comparison between the data for NaCl in Figure 4b to this droplet data.

Page 30, line 580: "AIOMFAC-VISC model sensitivity is defined by a 2% change in the aerosol water mass fraction, described in the supporting information of Gervasi et al. (2020)." Why is model sensitivity reported only from Figure 8 on and it is not reported in Figures 4 through 7? For completeness, I think it would be worth to add those in Figures 4 to 7 as well.

Page 30, line 588: "In both Fig. 8a,b there is one outlying data point at low  $a_w$  with a stated viscosity value at 108 Pa s. In fact, Song et al. (2021) used  $10^8$  Pa s as the upper limit for their viscosity measurements. Such a high value reported may be best explained by the crystallization of  $\text{Ca}(\text{NO}_3)_2$  or  $\text{Mg}(\text{NO}_3)_2$ , but using the poke-and-flow measurement technique, it is difficult to distinguish between glasses, gels, and crystallized aerosols." Are these points at  $10^8$  Pa s included in the fitting of the AIOMFAC-VISC model? Both in the case that  $\text{Ca}(\text{NO}_3)_2$  or  $\text{Mg}(\text{NO}_3)_2$  are either crystallized at that  $a_w$  or that the upper detection limit for viscosity was hit with the experiments by Song et al., it does not seem like this point should be included in the fit. If it is included indeed, can the authors explain their decision? Do the authors think that this could cause some bias in the fitting of the coefficients for the Ca, NO<sub>3</sub> and Mg ions?

Page 30, line 595: "At  $a_w < 0.2$ , the uncertainty of the AIOMFAC-VISC prediction for  $\text{NaNO}_3$  widens considerably, indicating that small changes in solution water content can greatly affect both the water activity and viscosity predictions. Indeed, a 2% change in mass fraction of water corresponds to a much larger change in water activity for  $\text{NaNO}_3$  (Fig. 6b) than for  $\text{Ca}(\text{NO}_3)_2$  (Fig. 6e) or  $\text{Mg}(\text{NO}_3)_2$  (Fig. 6g)." Would it be worth to add a quick figure in the supplement to show plots of mass fraction vs.  $a_w$  for these different systems to guide the reader through this reasoning?

Page 30, line 601 and following. I think the discussion of the cases where crystallization or gel formation is missing an important point. Taking  $\text{MgSO}_4$  as an example, predictions of viscosity below  $a_w=0.4$  do not seem to be "physical" considering the measurements of Richards et al., who observed gel formation and no relaxation whatsoever of the coalesced droplets over a really long timescale. Similarly, that is also the case for the prediction of the viscosity for other binary electrolytes that crystallize at a specific RH. What is the viscosity of a crystalline solid or a gel? My guess is that the authors have included the predictions for crystalline solids and gels because if one was to make simulations for more complex mixtures that included electrolytes that in their binary solutions would be either a solid or a gel at that specific  $a_w$ , it is not necessarily true that this hypothetical more complex mixture would also be crystalline/gel-like (which discussed in Page 32, paragraph starting at line 633). Is this the case or are there other reasons why the authors have included predictions for solids or gels, instead of for example prevent the model to provide a prediction of viscosity for those cases? I think this is an important aspect of the

presented modelling approach that should be discussed more explicitly.

Page 32, line 634: "while the ZSR-style mixing rule performs best for 1:1 sucrose-Mg(NO<sub>3</sub>)<sub>2</sub> (Fig. 10b) and 635 80:20 sucrose-NaNO<sub>3</sub> (Fig. 10d)". Given the error bars for both measurements and models in these figures, I would argue that the ZSR-like model and the aquelec model have similar performances for these two cases. Could the authors please either revisit the statement or provide some quantitative metric to support this statement?

Page 32, line 646: "In terms of computational speed, the ZSR mixing model takes approximately five to six times longer than aquelec or aquorg (see Tables S1 and S2 in the SI.". Could the authors please provide timescales for these simulations? I get the argument they are making about repeated calls for example in kinetic multilayer models, but I think it would be good to indicate whether the difference is for example between 0.01 and 0.05 s, or say 10 and 50 s. Also, there is a missing closing parentheses.

Page 35, Figure 11. Can the authors comment on the behaviour of the predicted viscosity of the organic-rich phase in Figure 11a at high  $a_w$ ? Viscosity seems to steeply increase going towards  $a_w=1$  and then even more steeply decrease towards the viscosity of water. Where is this trend originating from? The same trend seems to be also reproduced in Figure 12a.

Page 35, line 693: "We calculated the viscosities of the two phases for each vertical profile assuming the particles to be in equilibrium with the measured environmental conditions (T, RH) at each altitude level (which is unlike the case of an adiabatically lifted air parcel)". To be a little more explicit and for the sake of completeness, I think it might be useful to remind the reader here that water diffusion (as well as the diffusion of other species) is increasingly limited with increasing viscosity, which would affect the equilibration timescales in the case of an adiabatically lifted air parcel.