Authors' responses to referee comments on Lilek and Zuend manuscript

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We would like to thank the three referees for their interest in our manuscript and for providing helpful comments and suggestions. In this document, we have repeated the referee comments (in black font) followed by our responses in red font. Changes to the manuscript related to the comments are also indicated, with page and line numbers listed referring to those from the original manuscript.

Response to Referee 1

- 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.

Thank you for your positive view of this manuscript and your comments. To your first point, we opted to include viscosity predictions covering the range from dilute to highly concentrated electrolyte solutions, even if such predictions at higher concentration may go beyond the crystallization or gel transition limits. We have two reasons for this choice: the primary reason is to provide physically reasonable predictions of viscosity for any (single-phase) mixture that is specified at input regardless of whether it refers to an equilibrium or a non-equilibrium state of a system. The non-equilibrium states could be metastable, such as in supersaturated salt solutions that occur in atmospheric aerosols, or they could refer to an unstable state, which is difficult to generate in an experiment. The second reason has been mentioned by the referee: for a model to provide predictions for more complex mixtures of various ions as well as inorganic–organic mixtures, covering a larger range in ionic strengths than had been used in the training of the model based on experimental data, we need to make sure that the extrapolations of the viscosity predictions toward higher concentrations do not behave nonphysically (e.g. prevent negative values or sharp changes). Both reasons are perfectly in line with the aim of the AIOMFAC model of predicting activity coefficients for any given input composition, since at its core AIOMFAC is a non-ideal mixing model, not an equilibrium model. AIOMFAC solutions only refer to the equilibrium state if the input composition leads to a single-phase solution at equilibrium (while partial dissociation of certain ions, such as HSO_4^-, is accounted for).

Thermodynamic equilibrium models can be built based on AIOMFAC, which will then provide the equilibrium liquid-state compositions for which AIOMFAC-VISC can be run. This includes consideration of liquid–liquid and solid–liquid equilibria on the composition of the remaining (viscous) liquid phases – and in the future may cover gel transition effects.

Regarding suggestions for further viscosity measurements to better constrain the model, we refer to our responses related to this point below (specific comments 3 and 7).

- 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.

1. 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.

We agree with this revised order and have modified the introduction accordingly. Changes are detailed below.

Changes to the manuscript:
Page 3, line 80. Section 1.3 "Our model: AIOMFAC-VISC" has been renamed "Viscosity predictions in AIOMFAC; the AIOMFAC-VISC model" and is now Section 1.2. The sentence beginning at line 88 has been modified and moved to the beginning of Sect. 1.3. Section 1.2 "Two popular frameworks" (which starts at Page 3, line 53) is now Sect. 1.3.

2. 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 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?

   AIOMFAC uses the terminology and definition following the work by Yan et al. (1999), in which organic components and water are called "solvents" and the term "solute" refers to ions. For this reason, ion molalities (or any molalities) are defined as moles of species per 1 kg of solvent mixture. We have added this reference to the text. One key reason for such a perhaps less common definition of molality is that in mixed organic–inorganic systems water may not even be present when ions are, e.g. in certain ethanol + ion systems (Zuend et al., 2008), while molality of the ions still needs to be properly defined and calculable. Using the solvent mixture mass in the denominator of the molality expression achieves this. Note that regardless of this definition of molality, in AIOMFAC the reference solvent for ions is pure water (which matters for the definition of ion activity coefficients).

   Changes to the manuscript:
   Page 5, line 134: Added text "Following the terminology and definition given by Yan et al. (1999),"

3. Page 10, line 240: "More recently, techniques such as poke-and-flow, bead mobility, and holographic optical tweezers 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.

   We agree with this point. Recent measurements of organic–inorganic mixtures using droplet-based techniques, including those by Rovelli et al. (2019), Richards et al. (2020b), and Song et al. (2021), suggest continuing interest in pursuing additional measurements. This has been confirmed in personal communication with our experimentalist colleagues. We have added references to this in the text to provide context.

Changes to the manuscript:
On Page 10, line 249, we added supporting references to these sentences and slightly rephrased as: "More recently, techniques such as poke-and-flow, bead mobility, and holographic optical tweezers have enabled viscosity measurements for droplets (Reid et al., 2018). Due to their small size and/or 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 (e.g., Rovelli et al., 2019; Richards et al., 2020a,b; Song et al., 2021). Viscosity measurements obtained at high electrolyte concentrations are of value for the development of models like AIOMFAC-VISC to improve and/or validate predictions in this less frequently measured composition range of atmospheric relevance."

4. Page 20, line 493: "Two systems stand out, however: NaNO3 and Ca(NO3)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. NaNO3 and Ca(NO3)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.

   The higher-range viscosity values are 10^1 and 10^2 Pa s, which were observed in droplet-based measurements collected by Baldelli et al. (2016) and Song et al. (2021). We appreciate this suggestion and have added these numbers and a mention of Fig. 8 into the text.

   Changes to the manuscript:
   Page 20, line 493: Changed to "These two systems include some of the highest viscosity values among the available measurements (e.g., 10^1 to 10^2 Pa s), which is a factor in their large contributions to the overall objective function error. $NaNO_3$ and $Ca(NO_3)_2$ also include both bulk and droplet-based measurements, and these data do not agree with each other at low water content, leading to larger fit residuals for these systems – see Fig. 8."

5. 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?

   The stepwise appearance of the two bottom panels is due to the dense clustering of measurements – the pattern appears stepwise because columns corresponding to different solution compositions at similar mass fractions of water. The alternative would be to make each column so thin as to be effectively invisible, so we believed that this was the best way to show the data. This system includes measurements with

$CaCl_2$ and NaCl in varying proportions (for some at similar water mass fraction); thus, such mixture data are unlike those for binary systems, for which smooth curves can be plotted. Also, as is the case for most bulk viscosity measurements shown in our manuscript, the data come from multiple sources (explained in Tables 2–4).

Changes to the manuscript:
We have slightly reduced the width of the bars in Fig 3a.

6. 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.

   We agree that this phrasing is unclear, and we have removed this sentence.

   Changes to the manuscript:
   Page 24, line 526: The sentence was removed.

7. 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.

   Thank you for this important suggestion. We have compared model performance with parameters fitted from both binary and multi-ion measurements and from only binary measurements. We have created a supplemental figure (shown below) showing this comparison and have included additional discussion in this section.

   Changes to the manuscript:
   After Page 25, line 541, added "In fitting the AIOMFAC-VISC electrolyte model, we chose to use all data sets that were available and accessible, including aqueous mixtures

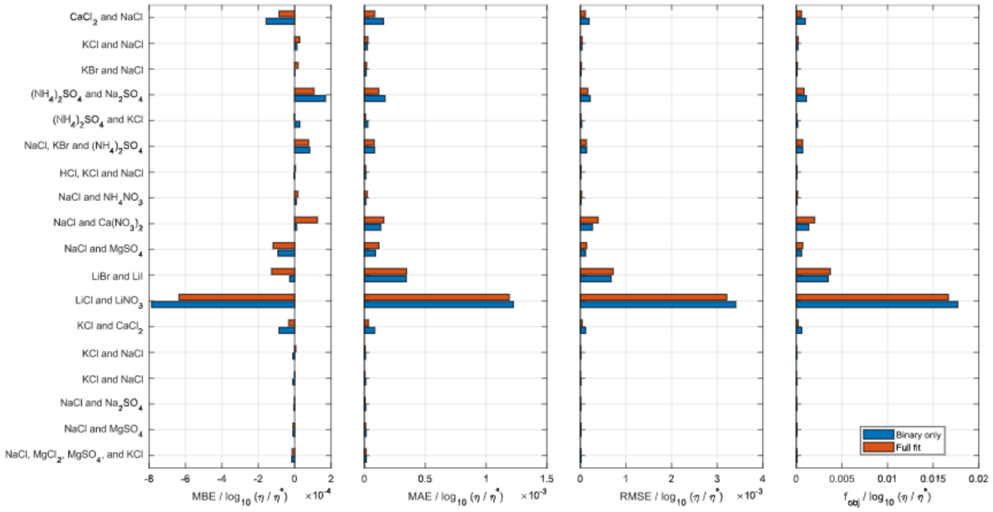

Figure S6. Comparison of the model–measurement error of AIOMFAC-VISC when using parameters fitted to only binary data (blue) versus to all available data (red): (a) mean bias error, (b) mean absolute error, (c) root mean square error, and (d) custom objective function value used to fit AIOMFAC-VISC. See Table 3 for information on number of data points, the ranges of temperature, concentration, and viscosity for each data set. η° denotes unit viscosity (1 Pa s). See also Fig. 1.

of more than one electrolyte. Most of the model parameters are well constrained by the binary electrolyte solution data, although two cation–anion interactions, namely NH_4^+–Br^- and Li^+–I^-, are fitted exclusively based on ternary mixture data because binary mixture data were not available. In comparing the performance of the AIOMFAC-VISC electrolyte model using all available data versus only binary mixture data considering overall fit quality metrics, the model improves slightly when the multi-ion data are included; see Fig. S6. To further improve the model, we believe that viscosity measurements at higher electrolyte concentrations will be more helpful than measurements of multi-ion mixtures at dilute conditions. The advent of droplet-based measurements, which can probe higher concentration ranges, will be especially useful in this area. For further discussion of this, see Sect. S5."

8. 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.

   Pure water has a plasticizing effect on viscosity. For this reason, the viscosity of aqueous electrolyte solutions is smaller/closer to the viscosity of pure water at high mass fractions of water. As the mass fraction of water approaches zero, water is expected to be contained mostly in tightly held temporary hydration shells. For structure-making ions in particular, these hydration shells increase the effective volume of the ions, making it more difficult for ions to flow past one another. In addition, electrostatic attraction among cations and anions can lead to the formation of cation–anion pairs that move together, further impeding the flow of the mixture (if crystallization has not occurred at that point). In AIOMFAC-VISC, these impedances to flow are represented by different contributions to the Gibbs energy of activation for viscous flow. When the mass fraction of water is zero, the predicted result is essentially a supersaturated ionic liquid. However, under atmospheric conditions, such a mixture would usually crystallize before this state is reached.

The Laliberté model has a different functional form than AIOMFAC-VISC and more adjustable parameters, ensuring a closer fit to the (bulk solution) measurements in the range where those are available. However, Laliberté (2007) notes, "Extrapolating by 10 % to 20 % over the maximum concentration where data are available is probably acceptable for many applications. Above this, the error increases rapidly and the predicted viscosity is lower than its actual value. [Except for cases where the solute decreases the viscosity of the solution, in which case the predicted solution viscosity will be higher than its actual value.]"

The steep increase in viscosity at low mass fraction of water is likely due to higher relative influence of the ionic-strength-dependent cation–anion viscosity contributions, as mentioned in reference to chloride salts in Fig. 4.

Changes to the manuscript:

On page 19, line 486, we added "As will be shown later in Sect. 4.5, a related drawback of the Laliberté model is occasional spurious behavior when extrapolating outside of the range of available measurements."

9. Page 30, Figure 8: Power et al. (Power, R. M., Simpson, S. H., Reid, J. P. and 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 aw=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.

   A refit of the model would be necessary to include this data, but these data do not appear to be available in tabulated form. However, the Power et al. (2013) data appear to fit within the bulk viscosity measurements aggregated by Laliberté (2007). We had similarly wished to include the ternary mixture data of sucrose + NaCl in this article, but tabulated data was not available. The binary aqueous NaCl prediction from AIOMFAC-VISC slightly underpredicts the binary water + NaCl measurements at the lowest mass fraction of water of about 0.7 – see Fig. 2.

   Note that the bulk measurement data for binary aqueous NaCl solutions includes substantial spread. Also, as Power et al. (2013) state that their measurements were

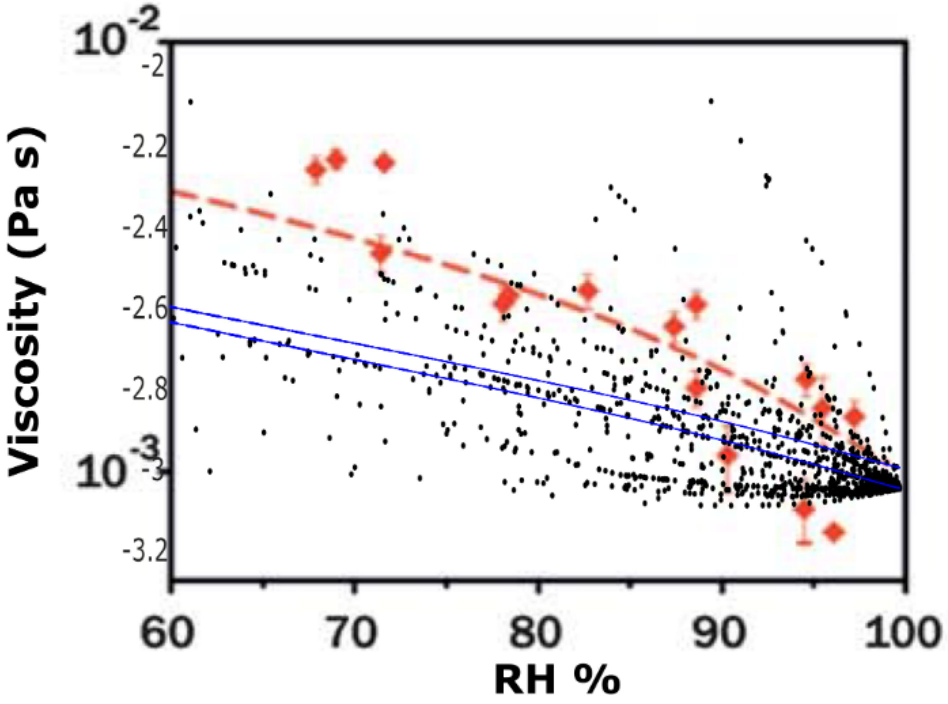

Figure S12. AIOMFAC-predicted viscosity for binary NaCl (blue solid curves) and bulk measurements (black dots) overlaid on droplet-based measurements (red diamonds) and ADDEM model prediction (red dashed curve) from the inset of Fig. 3a in Power et al. (2013). Power et al. (2013) state that their measurements were completed at "room temperature" but do not otherwise specify the precise temperature, so we have included bulk measurements from 293 to 298 K and AIOMFAC-VISC model curves for 293 and 298 K as upper and lower bounds, respectively.

completed at "room temperature" but do not otherwise specify the precise temperature, we have included bulk measurements from 293 to 298 K and AIOMFAC-VISC model curves for 293 and 298 K as upper and lower bounds, respectively.

Changes to the manuscript:
We added a supplemental figure (Fig. S12) comparing AIOMFAC-VISC predictions with the droplet-based measurements (and model) for binary aqueous NaCl from Power et al. (2013).

10. 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.

    We agree, and we have generated new versions of the figures that include model sensitivity.

    Changes to the manuscript:
    Figures have been updated with sensitivity curves; related text has been added to the affected figure captions.

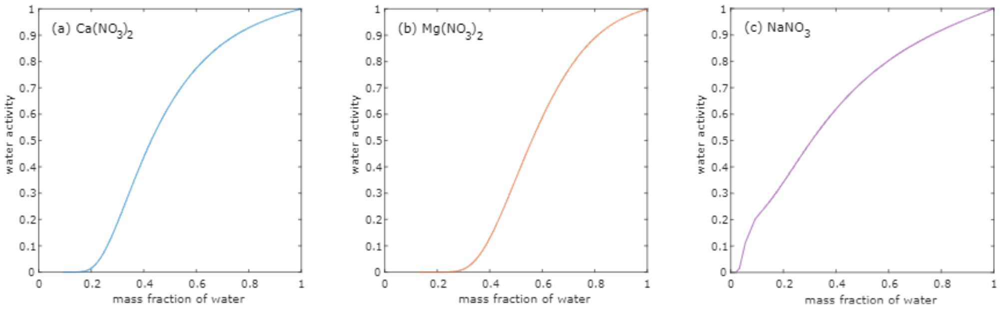

Figure S11. Mass fraction of water versus AIOMFAC-predicted water activity for binary aqueous nitrate solutions. Panels correspond to those of Fig. 8.

11. Page 30, line 588: “In both Fig. 8a,b there is one outlying data point at low aw 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 Ca(NO3)2 or Mg(NO3)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 Ca(NO3)2 or Mg(NO3)2 are either crystallized at that aw 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, NO3 and Mg ions?

   The point was not included in the model fit, and we have clarified this in the figure caption. As this referee mentioned, we believe the inclusion of those data points would have biased the coefficients of those ions. We also assume that those points are likely explained by the crystallization of the salts at those low water contents.

12. Page 30, line 595: “At aw < 0.2, the uncertainty of the AIOMFAC-VISC prediction for NaNO3 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 NaNO3 (Fig. 6b) than for Ca(NO3)2 (Fig. 6e) or Mg(NO3)2 (Fig. 6g).” Would it be worth to add a quick figure in the supplement to show plots of mass fraction vs. aw for these different systems to guide the reader through this reasoning?

   We appreciate the suggestion and have added such a figure to the supplement, referring to it in the main text.

   Changes to the manuscript:
   Figure S11 added to the supplement.

13. Page 30, line 601 and following. I think the discussion of the cases where crystallization or gel formation is missing an important point. Taking MgSO4 as an example,

predictions of viscosity below aw=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 aw, 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.

As Referee 2 notes, there is presently limited data for efflorescence and/or gel transitions of relevant mixtures. In the absence of these measurements, we believe that enabling viscosity predictions of single viscous liquid-state phases, even in the concentration ranges that appear nonphysical, is a useful approach. This is similar to the approach of the Laliberté model, which includes a function that can give an output for a mass fraction of water of zero (although Laliberté cautions that extrapolating too far beyond the measured concentration range for each salt solution can result in unreliable viscosity values). A primary goal of a AIOMFAC-VISC calculation is to provide a prediction of mixture viscosity for a given input composition regardless of whether that composition represents an equilibrium or non-equilibrium state of mixing (including consideration of metastable, supersaturated electrolyte solutions). This is in line with the purpose of the AIOMFAC core model for activity coefficient predictions of given mixtures. Moreover, thermodynamic equilibrium models based on AIOMFAC can be used to predict phase compositions at liquid–liquid, gas–liquid and/or solid–liquid equilibrium, which in turn can be used to provide viscosity predictions for each "liquid" phase separately, as done in the application examples of Figs. 11–13. Consideration of the viscosity of a gel state is beyond the scope of the current study and may be addressed in future work.

Changes to the manuscript:
Added "As we note above, efflorescence or a phase transition is expected in many binary aqueous electrolyte systems, which would seem to render a viscosity prediction purely theoretical. However, it is nevertheless valuable to generate output for these systems. Supersaturated liquids can exist in equilibrium without crystallizing. Furthermore, some mixtures include more than a single dissolved electrolyte and it is possible that a liquid containing a single solute would crystallize while a liquid containing high concentrations of multiple solutes would not."

14. Page 32, line 634: "while the ZSR-style mixing rule performs best for 1:1 sucrose–Mg(NO3)2 (Fig. 10b) and 80:20 sucrose–NaNO3 (Fig. 10d)". Given the error bars for both measurements and models in these figures, I would argue that the ZSR-like model and

the aqualec 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?

We have modified the statement to note the similar performance of the ZSR and aquelec mixing models for Fig 10b,d.

Changes to the manuscript:
Changed sentence to "The aquelec mixing model predictions appear to agree best with the measurements for 1:1 sucrose–$Ca(NO_3)_2$ (Fig. 10a) and 60:40 sucrose–$NaNO_3$ (Fig. 10c), while the ZSR-style mixing rule and aquelec perform similarly for 1:1 sucrose–$Mg(NO_3)_2$ (Fig. 10b) and 80:20 sucrose–$NaNO_3$ (Fig. 10d) when uncertainties in measurements and model predictions are accounted for."

15. 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.

    Table S2 provides the data the referee is interested in. The mean absolute time for a single mixture computation is on the order of a few tens of microseconds with a current CPU; however, actual times will differ depending on the type of CPU used, making a statement about the absolute computation time less useful. We have fixed the closing parenthesis.

    Changes to the manuscript:
    Page 32, line 646: missing closing parenthesis added.

16. 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 aw? Viscosity seems to steeply increase going towards aw=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.

    An explanation of this phenomenon has been added to the discussion of Fig. 11.

    Changes to the manuscript:
    At page 35, line 678, replaced "The surrogate mixture representing α-pinene SOA is listed in Table S4 of the SI" with "The surrogate mixture representing α-pinene SOA, defined in Table S4, consists of compounds that span a range of polarities and miscibilities with water and electrolytes. This explains an abrupt local maximum in the predicted organic-rich phase viscosity. As a_w values approach and exceed 0.98, this is accompanied by relatively large water uptake, and the liquid–liquid partitioning of the organic compounds changes substantially. Most of the moderately water-soluble organics partition to the aqueous ion-rich phase; only the least polar organics remain in the now depleted organic-rich phase. The remaining organic-rich phase includes dimers and a smaller water content, which leads to an increase in the predicted viscosity of

that phase. As even higher a_w values are reached, all compounds become miscible in a single, water-rich liquid phase, which has a viscosity close to that of pure water."

17. 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.

    Thanks for this suggestion. We have included text to that effect.

    Changes to the manuscript:
    At page 35, line 695 we removed "(which is unlike the case of an adiabatically lifted air parcel)," and added "This is unlike the case of an adiabatically lifted air parcel, for which the temperature and RH may substantially differ from those of its environment. It is worth noting that as viscosity increases, diffusion of water and other species is increasingly limited, which could affect equilibration timescales during adiabatic ascent, especially at high altitudes."

References

1. Yan, W., Topphoff, M., Rose, C., and Gmehling, J.: Prediction of vapor–liquid equilibria in mixed-solvent electrolyte systems using the groupcontribution concept, Fluid Phase Equilibria, 162, 97–113, https://doi.org/10.1016/S0378-3812(99)00201-0, 1999.

Response to Referee 2

- This manuscript describes an exciting extension of the AIOMFAC-VISC model. AIOMFAC and AIOMFAC-VISC are models that are extensively used in the aerosol community. Until now, AIOMFAC-VISC could not perform viscosity prediction for systems other than binary organic/water. Since atmospheric aerosol particles are mixtures of organic and inorganic compounds, extending AIOMFAC-VISC to include more complex mixtures will be very beneficial.

  Thank you for your comments. We would like to clarify here that the aqueous organic viscosity model introduced by Gervasi et al. (2020) is capable of predicting viscosity for mixtures of water and an arbitrary number of organic components, as opposed to only binary mixtures of water and one organic component.

- General comments:

  The new extension presented here is shown to work exceptionally well for both water/electrolyte and water/electrolyte/organic systems. The manuscript is accessible, even without a background in thermodynamic modeling. The authors certainly put in the effort to explain the justifications. I have no major concerns; the agreement between measurements and AIOMFAC-VISC are suggestive of the broad applicability, authors are forthright regarding the limitations of the model as well as the fact that there are a limited number of data sets to compare model predictions to. I recommend publication of this manuscript, which will be a tremendous resource to the aerosol community.

- Anonymous Referee 1 raises an excellent point about “unphysical” predictions regarding crystallization and gelation. However, I will note that this aspect of the model may actually be particularly helpful at identifying gel/ efflorescence transitions in measurements based on deviations from the model. For example, MgSO4 is known to form a gel at water activity of 0.3. At this water activity, AIOMFAC-VISC predicts a viscosity of 10^4 Pa s (from Fig. 5 of the manuscript). In Richards et al. (2020a), MgSO4 was observed to be entirely rigid at a water activity of 0.3, which is not consistent with a viscosity of 10^4 Pa s. This discrepancy further supports the notion of a gel transition. Similarly, the discrepancies between experiment and model in Figure 8 of the manuscript, where viscosity measurements of Mg(NO3)2 and Ca(NO3)2 were compared to AIOMFAC-VISC predictions, reinforce the supposition that efflorescence, or some form of phase transition, had occurred in measurements.

  I do not believe this to necessarily be a problem with the model. Rather, it is something the community should be aware of when interpreting model predictions. Efflorescence is difficult to predict without observations, and even then can occur across a range of RH (in principle, as high the deliquescence RH). Similarly, not enough is known about gel-forming systems at this point to identify any gelation point where the model becomes unphysical. Richards et al. (2020b) has some limited observations involving CaCl2 and organics. Nadler (2018) also suggests a gel transition in CaCl2-sucrose systems at 26-28 % RH. Lv et al. (2018) showed gelation in magnesium acetate at $<$ 50 % RH. In other words, the available observations are quite sparse. Unless/ until there are more measurements on gel transitions/ efflorescence of all potential mixtures, the presented version of AIOMFAC-VISC is possibly the most helpful.

Thank you for this added context. We have noted this comment in our response to the feedback from Referee 1.

Minor comments on formatting, presentation, clarity, etc.

1. In Figures 4- 7, is there any particular reason all of the y-axes extend to 10^8 Pa s? For some systems, e.g., Fig. 7a (KBr), which has a maximum value of 1 Pa s, it becomes difficult to see any differences because the values appear effectively flat relative to the large scale.

   As you say, extending the y-axes to 10^9 Pa s can make it difficult to see the differences in the range of the actual measurements, which would provide valuable information about the model performance. For this reason, we have changed the upper y-axis limit in Figs. 4-7 to 10^3 Pa s. For aerosol applications, viscosity differences of less than 1 mPa s are typically not very important, as opposed to differences of one or more orders of magnitude above the liquid range ($> 10^2$ Pa s). We have also included zoomed in versions of Figs. 5-7 in the supplement and add references to these supplemental figures in the figure captions.

   Changes to the manuscript:
   We have added new supplemental figures showing enhanced zoom on the measurement data points. The upper y-axis limit on Figures 4-7 has been changed to 10^3 Pa s.

2. My other comments on presentation/ clarity have already been covered by Referee 1, so I will not reiterate those here.

References

1. Xi-Juan Lv, Yang Wang, Chen Cai, Shu-Feng Pang, Jia-Bi Ma, Yun-Hong Zhang, Investigation of gel formation and volatilization of acetate acid in magnesium acetate droplets by the optical tweezers, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 200, 2018, https://doi.org/10.1016/j.saa.2018.04.027.

2. Nadler, Katherine Adele. Application of a Mobile Electrodynamic Balance for Studying Water Diffusion in Single Charged Aerosol. PhD Thesis.
   https://escholarship.org/uc/item/27z907g1

   Data/discussion on CaCl2-sucrose on pages 157-158.

3. Richards, D. S., Trobaugh, K. L., Hajek-Herrera, J., and Davis, R. D.: Dual-Balance Electrodynamic Trap as a Microanalytical Tool for Identifying Gel Transitions and Viscous Properties of Levitated Aerosol Particles, Analytical Chemistry, 92, 3086–3094, 890 https://doi.org/10.1021/acs.analchem.9b04487, 2020a.

4. Richards, D. S., Trobaugh, K. L., Hajek-Herrera, J., Price, C. L., Sheldon, C. S., Davies, J. F., and Davis, R. D.: Ion-molecule interactions enable unexpected phase transitions in organic-inorganic aerosol, Science Advances, 6, eabb5643,

https://doi.org/10.1126/sciadv.abb5643,
https://advances.sciencemag.org/content/6/47/eabb5643, 2020b.

Response to Referee 3

- This is the review for the manuscript entitled "A predictive viscosity model for aqueous electrolytes and mixed organic–inorganic aerosol phases" by Lilek and Zuend.

  This manuscript describes an extension of the thermodynamics-based group-contribution model AIOMFAC-VISC to predict viscosity for aqueous electrolyte solutions and aqueous organic–inorganic mixtures. Viscosity is described by implementation of the activation energy for viscous flow following Eyring's equations for absolute rate theory. The viscosity information of close to 30 electrolytes (inorganic salts) were fitted simultaneously with AIOMFAC ion-specific expressions. Three different approaches were examined to describe viscosity of organic-inorganic mixtures. Lastly, an example is given how AIOMFAC-VISC can be applied to predict viscosity for phase separated organic-inorganic particles.

  The manuscript is well written, and its topic fits the research areas covered by Atmospheric Chemistry and Physics. I do not have major comments or revision requests, only minor comments the authors might consider before publishing the manuscript.

  In general, it might be beneficial to better integrate discussion of data shown in supplement into the main text. Some supplemental data show, e.g., that it is not always clear if AIOMFAC-VISC performs better than the Laliberte model and the reasons could be pointed out in main text. Additional viscosity data for organic-inorganic mixtures in supplement appear to not be predicted as well by AIOMFAC-VISC. Gel formation, phase transitions are mentioned as a cause but not within the place of the discussion of these data.

  Thank you for your comments. We have included additional discussion of the supplemental data regarding comparisons to the Laliberté model and gel transitions. Additions are described below in response to specific comments.

  Reading some of the sections, it occurred to me if there is a relation to the Hofmeister series (kosmotropes/chaotropes)? Just a comment.

  Thank you for sharing this interesting comment. We believe that there are different effects from structure-breaking and structure-making ions under dilute conditions; the presence of a structure-breaking ion (e.g., K^+) is often indicated by a local minimum in viscosity in the dilute range. Outside of the dilute range, viscosity of aqueous electrolyte solutions increases as a function of ionic strength.

1. l. 175: When reading this equation, the first question which came up in my mind is about the impact of hydration shell, shielding of ions, etc. This is addressed in the following section but how exactly was not clear to me. How does the hydrated volume impact the viscosity parameters/prediction? At that point in text, the mathematical link was not entirely clear. Also, around l. 175, one may want to make a note that hydration effects will be discussed in the next section.

   Hydration effects are only included directly insofar as they affect the effective relative van der Waals volumes of the ions. This is part of the separate V term, which is why they were not discussed in this section on Δg^*. An additional effect of the hydration of ions is indirectly accounted for by means of the single-ion activity coefficient values used in Eq. (13) from the AIOMFAC calculation. The way apparent hydration is treated in AIOMFAC is described in Zuend et al. (2008). We have added a remark about accounting for apparent ion hydration on line 165, where the ion activities are discussed.

Changes to the manuscript:
Line 165, before "Each cation–anion pair" we add the following sentences: "The partial or apparent hydration of certain ions in aqueous solutions are accounted for in a simplified manner when activity coefficients are computed with AIOMFAC. This is achieved by adjustments to the relative van der Waals volume and surface area values of affected ions, as detailed in Table 1 and in Zuend et al. (2008). Therefore, hydration effects are indirectly represented in the viscosity calculations via the ion activities and the ion contributions to the mean molar volume of a solution (Eq. 5); see also Sect. 2.4."

2. l. 511-513: Could "such as that for NH4Cl shown in Fig. 2d, the model is capable of reproducing the local minimum in measured viscosity." be shown in an extra figure in supplement?

   Yes, we have included such a figure in the revised supplement and refer to it in the main text. See Fig. S10 in this response. In this figure, all AIOMFAC-VISC parameters (i.e., for single ions and cation–anion pairs) were fitted using only bulk viscosity measurements of binary aqueous NH_4Cl solutions at 298 K.

   Changes to the manuscript:
   Figure S10 was added to the manuscript.

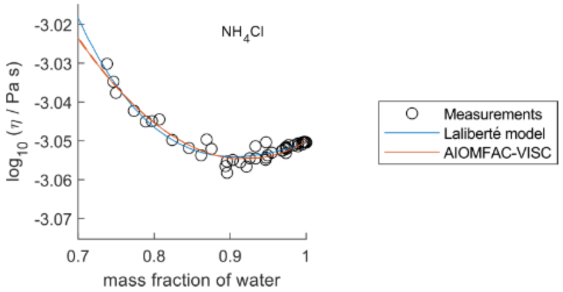

Figure S10. Comparison of the Laliberté model, AIOMFAC-VISC, and viscosity measurements versus mass fraction of water for NH_4Cl at 298 K when only binary NH_4Cl at 298 K was used to fit the model. Compare to result of simultaneous fit shown in Fig. 2d.

3. l. 532: I am not sure if I see that AIOMFAC-VISC outperforms the Laliberté model for 5 out of 6 points in Fig. 3b. For a mass fraction of water > 0.8, the models seem to perform similar. Below that amount of water, both models disagree with measurements (3 points) where AIOMFAC-VISC tends to be closer to the experimental data.

We agree that the models perform about equally well for the points where mass fraction of water > 0.8. AIOMFAC-VISC performs slightly better for the points below mass fraction of water $= 0.8$. We have clarified this in the text that the degree to which AIOMFAC-VISC outperforms Laliberté improves as ionic strength increases.

Changes to the manuscript:
At line 532, changed the sentence to "In Fig 3b, the number of data points is much smaller, but AIOMFAC-VISC outperforms the Laliberté model for the three points below mass fraction of water $= 0.8$, although both models predict slightly higher viscosities than measured. The two models perform equally well for the other three points."

4. l. 536 and following: More discussion should be given towards data in supplement. "AIOMFAC-VISC performs as well or better than the Laliberté model" does not mean that experimental data is reproduced. Likely, a more detailed discussion is needed.

   We agree, and we have added the following discussion of the ternary electrolyte mixtures.

   Changes to the manuscript:
   From line 537 to 539, we replaced the text with "In all but three of those multi-ion cases involving chloride, bromide, iodide, nitrate, sulfate, carbonate, bicarbonate, hydroxide, or any combination of these as anions, AIOMFAC-VISC performs as well or better than the Laliberté model (although this does not mean that the predictions reproduce the experimental data). The first exception is NaCl + $MgSO_4$ (Fig. S3a). However, the differences between the modelled viscosities in this case are less than 1 mPa s. The second is NaCl + $Ca(NO_3)_2$ (Fig. S1b), where AIOMFAC-VISC predicts a slightly higher viscosity than the Laliberté model for a measurement at $w_\mathrm{w} = 0.6$, driven by our decision to include the droplet-based measurements for aqueous $Ca(NO_3)_2$ in our fit, and these do not agree with the bulk measurements. The third is Na_2CO_3 + NaOH, where AIOMFAC-VISC predicts lower viscosities than measured due to underprediction of binary NaOH. Also, in several of the supplemental figures, multiple temperatures are shown, demonstrating the robustness of AIOMFAC-VISC's parameters. Given that the multi-ion data sets were used in the overall fit of the AIOMFAC-VISC parameters, this is not unexpected."

   For example:

   Fig. S1b, at low mass fraction of water, AIOMFAC-VISC yields higher viscosity.

   Indeed, but this is expected due to AIOMFAC-VISC including in the fit droplet-based measurements of aqueous Ca(NO3)2, which do not agree with the bulk measurements. We have noted this in the manuscript.

   Changes to the manuscript:
   Following line 537, added "The second is NaCl + $Ca(NO_3)_2$ (Fig. S1b), where AIOMFAC-VISC predicts a slightly higher viscosity than the Laliberté model for a measurement at $w_\mathrm{w} = 0.6$, driven by our decision to include the droplet-based measurements for aqueous $Ca(NO_3)_2$ in our fit, and these do not agree with the bulk measurements."

Fig. S1c, d: Is something missing in legend? Symbols and legend do not fit.

Thank you for catching this. In Fig. S1c, no Laliberté predictions exist because these electrolytes are not fitted by their model. In Fig. S1d, the color/symbol for AIOMFAC-VISC is incorrect and the legend entry for Laliberté is missing. We have fixed these mistakes.

Changes to the manuscript:
In Fig. S1c,d, we changed the legend entries to correspond to the data that is shown.

Fig. S3a: Is AIOMFAC-VISC doing consistently worse? It would appear so, and we have noted this in the text. This system from Nowlan et al. (1980) includes varying proportions of NaCl to MgSO4. When the proportion of MgSO4 is higher, AIOMFAC-VISC underpredicts the measurements, owing to its underprediction of binary aqueous MgSO4 in the current best version of the model parameterization. Note that AIOMFAC-VISC predicted viscosities agree with binary aqueous MgSO4 measurements at higher concentrations (not shown on the horizontal scale of this panel).

Changes to the manuscript:
At line 537, added "The first exception is NaCl + $MgSO_4$ (Fig. S3a). However, the differences between the modelled viscosities in this case are less than 1 mPa s."

5. l. 644-645: Results shown Figs. 6 and 7 are very interesting and should be more discussed in main text. The reasons for the discrepancy between 1:1 mixtures and predictions could be a bit more elaborated on.

   Thank you for this comment. We assume you are referring to Figs. S6 and S7. These figures show AIOMFAC-VISC mixture viscosity predictions compared to measurements from Richards et al. (2020b) for several 1:1 (mole ratio) mixtures of organics and inorganic salts containing a doubly charged ion (e.g., Ca^{2+}, Mg^{2+}, SO_4^{2-}). Richards et al. (2020b) identified gel transitions for these mixtures; gel formation is not included in the version of AIOMFAC-VISC described in this manuscript. We are considering the treatment of gel-forming mixtures with additional model terms in future work. Those extensions of the viscosity model will likely be mixture-specific. We have added additional discussion of these mixtures in manuscript.

   Changes to the manuscript:
   After line 645, added "Richards et al. (2020a, b) hypothesized that interactions between doubly charged ions (especially cations) and certain organic compounds can lead to the formation of a gelatinous network that would have different rheological properties than a viscous liquid. Indeed, the discrepancies between the AIOMFAC-VISC predictions and these measurements may in itself be evidence of a gel transition for these systems. Of the seven organic–inorganic mixtures shown in the supplemental figures, only a mixture of $(NH_4)_2SO_4$ and gluconic acid is reasonably represented by AIOMFAC-VISC, suggesting that the gel-forming ability of $(NH_4)_2SO_4$ is weaker than that of the other electrolytes shown. As in Fig. 8a,b, the measurement point reported for the lowest RH is given as a lower bound estimate of the viscosity and the upper vertical error bar is unbounded. In the supplemental figures, these points are meant to indicate a discrete change in behavior from a viscous liquid to a gel."

6. l. 679 and following: Discussion of Fig. 12. Data for phase states of SOA and SOA with sulfates as a function of temperature and humidity are scarce. Suggestion: data shown in Fig. 12 could be set in context with the experimental/theoretical study by (Charnawskas et al., 2017) who looked at water uptake and freezing of SOA, SOA+sulfates with respect to glass transition and full deliquescence relative humidity.

   Thank you for this suggestion. We have included a mention of the results from Charnawskas et al. (2017) in our discussion of Fig. 12.

   Changes to the manuscript:
   After line 690, added "Charnawskas et al. (2017) found that α-pinene SOA containing sulfate do not significantly impact ice formation in mixed phase clouds, basing their conclusion on chamber experiments and numerical diffusion modeling. According to the authors, heterogeneous ice nucleation of α-pinene SOA/sulfate particles would only occur below temperatures of approximately 222 K. Although the organic-rich phase of our α-pinene SOA/AS surrogate mixture can attain a glassy viscosity (i.e., 10^{12} Pa s) at temperatures as high as 265 K (when RH = 0 %), Charnawskas et al. (2017) considers that deliquescence may occur on these particles before a glassy viscosity is attained, in which case these particles would no longer be suitable for ice nucleation."

7. Technical corrections:

   l. 442: "is the data…" instead of "in the data"?

   Indeed. We have fixed this mistake.

   Changes to the manuscript:
   At line 442, we corrected the phrase "is the data" to "in the data."

References

1. Charnawskas, J. C., Alpert, P. A., Lambe, A. T., Berkemeier, T., O'Brien, R. E., Massoli, 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 interactions with implications for cold cloud formation, Faraday Discuss., 200, 164-195, 10.1039/C7FD00010C, 2017.
