**“Treatment of non-ideality in the multiphase model SPACCIM-Part2: Impacts on the multiphase chemical processing in deliquesced aerosol particles”** ***by*** **Ahmad J. Rusumdar et al.**

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**Anonymous Referee #2**

The authors present a sensitivity study of the impact of considering non-ideal solution effects on predictions of aqueous aerosol chemistry using the SPACCIM-SpactMod model. The study is well-conceived, and the results highlight the potential significance of non-ideal solution effects in multiphase atmospheric chemistry, something that is generally ignored in atmospheric models due in part to computational expense but also because of a lack of data. I think the manuscript will be suitable for publication in ACP after a few clarifications.

The authors thank reviewer 2 for the positive and thoughtful comments to improve the manuscript. The comments of the reviewer are carefully addressed point by point in the section below. The answers to the reviewer comments are marked as blue text. Moreover, all changes made in the manuscript are marked in the version with tracked changes.

- The aqueous chemical kinetic data in CAPRAM, which the multiphase chemical kinetic simulations in this study were based on, for the most part was not originally measured/reported as a function of activity but rather of concentration. The measurements that form the basis of that data were also mostly performed under much more dilute and closer to ideal conditions than the aqueous aerosol conditions considered here. How accurate is it to use those rate laws but plug in the activities calculated here - which are in many cases very different from the activities where the rates were originally measured both because of the high concentrations of atmospheric aerosols but also because of the non-ideality? Is it even possible to evaluate this?

Answer to the reviewer comment:
The reviewer is right that most of the kinetic reaction parameters are determined in the laboratory under much more dilute and closer to ideal conditions than aqueous aerosol conditions. Thus, effects of important parameters such as the ionic strength are not investigated by such studies and are therefore not considered in the current version of CAPRAM. However, the ionic strength is a main parameter in the calculation of the activity coefficients and consequently also in the calculation of the reactive fluxes.

Ionic strength effects are believed to be an important parameter of particle chemical reactions such as S(IV) oxidation (Martin and Hill, 1987; Lagrange et al., 1993; Lagrange et al., 1994; Maaß et al., 1999; Ali et al., 2014; Cheng et al., 2016), although experimental data at the extremely high ionic strengths typical of atmospheric aerosols are limited. Studies available studying the ionic strength effects (see e.g. Weller et al. (2010) and Herrmann et al. (2015) and references therein), however, often only quantify the overall effect of both ionic strength and the activity coefficients. To provide ionic-strength dependent reaction rate constants, the activity coefficients of the educts need to be considered to finally derive the single effect of the ionic strength. Such combined laboratory studies and model calculations would be a way to come up with datasets that can overcome the current model implementation limitation.

The current limitation in the applied mechanism is now briefly addressed in the revised manuscript in Sect.2.2. and reads as follows:

“Overall, it is worth to be noted that most of the kinetic reaction parameters considered in CAPRAM are determined in the laboratory under dilute and closer to ideal conditions rather than concentrated aqueous aerosol conditions. Thus, effects of important concentrated solution parameters such as ionic strength have not been investigated by such studies and are therefore not considered in the current version of CAPRAM. Once more ionic-strength dependent reaction rate constants become available, they have to be considered in future mechanisms."

- I agree with the other referee's comment that the uncertainty in the MR parameterizations for Fe and Mn are a significant weakness, especially given the likely importance of those two ions in multiphase atmospheric chemistry. Could the authors estimate those parameters, perhaps from available lab data, to at least constrain the effect?

Answer to the reviewer comment:
The authors fully agree with the reviewer that the missing middle range interaction parameters for Fe and Mg ions might weaken the conclusions of this study. The authors already thought about this issue quite a bit during the analysis of the modelled data. An educated guess to estimate those middle range interaction parameters was already discussed. For this reason, we have already compared available middle range interaction parameters of different metals. This comparison showed that also similar metals, for example $Mg^{2+}$ and $Ca^{2+}$ (same charge and main group in the periodic table), can be characterized by rather different middle range interaction parameters. Moreover, the use of the $Cu^{2+}$ interactions parameters for Fe and Mn ions can be also difficult as the chemistry of copper is known to be different from those of Fe and Mn. Nevertheless, according to the reviewer comment, we have included a new section in the SI comparing the base model runs with runs where the parameters for $Cu^{2+}$ have been applied for $Fe^{2+}$ and $Mn^{2+}$. A link to the sensitivity studies in the supplement is now included into the revised manuscript (see Sect. 3.4).

- Considerable uncertainty exists in the measured and reported rate data for much TMI chemistry, especially when it comes to ionic strength and pH dependence. Can the authors comment on the relative significance of these uncertainties to the non-ideal solution effects calculated here?

Answer to the reviewer comment:
The reviewer is certainly right that there are considerable uncertainties in available reaction rate data of the TMI chemistry and potential gaps exists in the scientific knowledge about their speciation, reactivity and complex interactions. The uncertainties and knowledge gaps are surely related to the complex dependencies of the TMI chemistry on the acidity and ionic strength (see Deguillaume et al. (2005) and references therein) and are able to affect different key chemical subsystems such as the HOx, organic and sulfur chemistry. CAPRAM contains already a rather complex TMI chemistry implementation which is far from being complete due to many gaps in the scientific knowledge. When better measured chemical rate constants of TMI reactions become available they definitely need to be integrated into upcoming CAPRAM mechanism versions.

Regarding the relative significance of the uncertainties compared to the non-ideal solution effects, the authors think that a more advanced TMI chemistry knowledge would be surely needed but effects of non-ideality will be definitely also play a key role due to the potential impact of activity coefficients on the reaction rates and speciation constants. Thus, laboratory future studies need to investigate important parameters such as the "middle range interaction" parameters of different TMI compounds as they can impact the overall rates by about 2 orders of magnitude depending on the non-ideality of the solution.

- How often in the simulation are the activity coefficients recalculated, i.e. as concentrations change in the aqueous phase? Does it happen at every timestep?

Answer to the reviewer comment:
In simulation, activity coefficients are calculated at each timestep. Further details about the implemented procedure is given in Rusumdar et al. (2016). According to the reviewer comment, we have slightly updated SPACCIM-SpactMod description in Sect. 2.1 and address this issue now in the revised manuscript.

- Since much depends in this study on the model chosen for activity coefficients, it would have been nice to see a sensitivity study of other popular approaches that could have been used instead. This is done somewhat in Table 3 and page, last paragraph. Given the sharp criticism presented, the discussion of Mao et al (2013) in this paragraph needs more elaboration (how do you know the implementation was 'incorrect'?), perhaps in the SI.

Answer to the reviewer comment:

1. A sensitivity study using other popular activity coefficient approaches (EAIM, …) that could have been applied instead of AIOMFAC is an excellent idea but beyond the scope of the present study. A comprehensive sensitivity study using other popular activity coefficient approaches will be definitely a gainful task for the future.

2. Unfortunately, most multiphase chemistry studies do not apply activity coefficients in their models or, if activity coefficients are considered, studies do often not provide the calculated activity coefficients in the publications. We did again a literature survey and have extended Table 3 with available data found and updated the discussion in Sect. 3.1.1. Nevertheless, presently no comprehensive comparison is possible.

3. In the study of Mao et al. (2013), an activity coefficient $\gamma$ of 0.01 was applied for $Fe^{3+}$ based on the lowest estimate from Millero and Woosley (2009). However, the lowest estimate in Millero and Woosley (2009) is $\ln(\gamma)=-2$, i.e. $\gamma$ should be 0.135. Thus, the decadic logarithm was used by Mao et al. (2013) instead of the natural logarithm. This issue is now outlined in the remarks of Table 3.

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