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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Diffusivity measurements of volatile organics in levitated viscous aerosol particles" *by* Sandra Bastelberger et al.

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The authors would like to thank Referee #1 for the recommendation for publication and the helpful comments and questions. We address Referee #1's comments in our response given below and will incorporate the corresponding changes in a revised version of our manuscript.

Referee #2 : 1) Page 14, Line 15-16. "it is evident from the sharp RH steps in Fig. 6 that there is no time delay between particle response and the model response". I

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suspect that there is a small time delay (on the order of tens of minutes) between particle response to RH and the model response, since previous research has shown that there is a kinetic limitation to water uptake in sucrose-water particles at low relative humidities. For clarity, I suggest the authors state the small time delay between particle response to RH and the model response (assuming there is one), and then argue that this small time delay is not important in the current experiments since this time delay is very short compared to the time needed for PEG to evaporate from the particles.

Authors' response: We will make the following changes to the manuscript: "It is evident from the sharp RH steps in Fig. 6 that there is little time delay between the particle response and the model response (blue curve). For the lowest RH, the response time is at the most ~ 15 min, which is very small compared to the timescales over which the diffusivity coefficients were determined (> 10 h). This validates the assumption that water diffusion is sufficiently fast and does not have to be treated explicitly under the experimental conditions considered in this study. "

Referee #1 : 2) Page 9.The authors list changes implemented to adapt the model to the sucrose/PEG-4/water-system. In a couple of places it would be useful to indicate the accuracy of these changes. Specifically for points 3-4 it would be helpful to state roughly the accuracy of the methods used to calculate water content and density if known. In addition, for point 5, the authors state "Assuming zero PEG-4 concentration at infinite distance from the particle". Please state the accuracy of this assumption if known.

Authors' response: The accuracy of point 3, which refers to the use of ZSR, cannot be tested throughout the whole concentration range. However, we performed several bulk water activity measurements for non-saturated solutions (with the accessible concentration range being $x_{suc} < 0.1$). For f_{PEG} < 0.6 the ZSR based calculated ternary solution molality of PEG-4 for a given a_w deviated from the true solution values by less than 8 $\%$. For f_{PEG} < 0.2, which is closer to our experimental range, the ZSR based calculated ternary solution molality of PEG-4 for a given a_w deviated

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from the true solution values by less than 3 %. In general, as we approach very small PEG-4 concentrations, we expect the accuracy of ZSR predictions to be given mainly by our knowledge of the molality of sucrose. Similarly (concerning point 4), a subset of the above mentioned non-saturated solutions were used to perform density measurements with a pycnometer that can be compared to the partial molar volumes approach. The room temperature pycnometer measurements agreed with partial molar volume predictions within 1 %.

We will add the following sentence to the description under point 3: "The accuracy of this estimation cannot be tested throughout the whole concentration range. However, we performed several bulk water activity measurements for non-saturated solutions (with the accessible concentration range being $x_{suc} < 0.1$). For f_{PEG} < 0.6 the ZSR based calculated ternary solution molality of PEG-4 for a given a_w deviated from the true solution values by less than 8 %. For f_{PEG} < 0.2, which is closer to our experimental range, the ZSR based calculated ternary solution molality of PEG-4 for a given a_w deviated from the true solution values by less than 3 %. In general, as we approach very small PEG-4 concentrations, we expect the accuracy of ZSR predictions to be given mainly by our knowledge of the molality of sucrose. "

We will also add to point 4: "For estimating the accuracy of this approach a subset of the non-saturated solutions discussed under 3. were used to perform density measurements with a pycnometer that can be compared to the partial molar volumes approach. The room temperature pycnometer measurements agreed with partial molar volume predictions within 1 % "

Point 5 was previously discussed in Huisman et al. (2013), section 2. Our flow rates can maintain a p_∞/p < 1 % (Zhang and Davis, 1987). We will make the following change to the manuscript: "...where $\mathcal{D}_g$ is the gas phase diffusion constant of PEG-4, x_n is the mole fraction of PEG-4 in shell n, γ_{PEG} is the activity of PEG-4 in the ternary system (see Appendix A3), p^0 is the pure component vapor pressure of PEG-4 and R is the

universal gas constant. The flow rates used in the experiments are sufficiently high to maintain the vapor pressure far from the particle, p_∞, at less than 1 $\%$ of the vapor pressure above the particle, justifying the assumption (Zhang and Davis, 1987).

References

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