

## ***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 #2 for the recommendation for publication and the helpful comments and questions. We address Referee #2's comments in our response given below and will incorporate the corresponding changes in a revised version of our manuscript.

Referee #2 : Is there a potential for a 'non zero' limiting partial pressure of the evaporating organic to bias any inferred diffusion coefficient in these experiments? I appreciate this might be very difficult to quantify, but please add to any appropriate

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references. One might expect this would only really be a problem for low viscosity states.

Authors' response: Due to the finite experimental observation time of the particle within the EDB, there will, strictly speaking, always be a very small amount of PEG-4 left within the particle at the end of the experiment, thereby causing a non-zero PEG-4 partial pressure. If the "leftover" concentration of PEG-4 at the end of an experiment was substantial, this could in principle bias the total particle size inferred from the shifts of the LED Mie resonances for previous times. However, for the following reasons we deem a potential bias of our inferred diffusion coefficients caused by a substantial non-zero partial pressure of PEG-4 at the end of our experiments unlikely:

- The particles were equilibrated in the non condensed-phase diffusion limited regime until no shrinkage due to evaporation was observable. Given a 24 h observation period, our limit of sensitivity to radius change corresponds to a partial pressure of  $\sim 3.6 \times 10^{-7}$  Pa (Huisman et al., 2013). Under the assumption of ideality, this corresponds to  $x_{PEG} \sim 4 \times 10^{-5}$  in a homogeneous particle at 19.5 °C. Thus, we do not expect a large error in total radius due to a residual non-zero partial pressure at the end of an experiment.
- $f_{PEG}$ , i.e. PEG-4 content at the beginning of the experiment calculated from the Mie resonance shifts and the end size is consistent with the  $f_{PEG}$  of the solutions that were prepared to generate the particles.
- The retrieval of the PEG-4 condensed phase diffusivities relies on the rate of radius change and is not primarily dependent on the total radius.

Referee #2 : I am a little confused by the comment in point '2' on page 9 that you assume the condensed phase diffusion of PEG to not rely on its own concentration?

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Given the mixture composition will dictate the changing viscosity, doesn't this restrict the use of your fit in other studies? Or, is it that you are targeting the use of your fit in other mixtures where you only need to track water?

Authors' response: The diffusivity retrieval in this study relies on the simplifying assumption, i.e. Fickian diffusion (the diffusivity is independent of concentration of PEG-4), that can be made in the limit of the low concentrations of PEG-4 that were used. This approach will indeed break down for higher PEG-4 concentrations, which inherently necessitate a much more complicated treatment, i.e. solving the nonlinear diffusion equation. Hence, instead of covering the whole concentration range, this study aims at providing diffusivity measurements for a PEG-4 like molecule in the viscosity range we investigated. To clarify which viscosity range was addressed, we will make the following changes to the manuscript: "Bosse ideal mixing yields good results for aqueous sucrose and suggests that, if applicable to our ternary system, sucrose provides the dominant contribution to the mixture viscosity due to its very high "pure component" viscosity and the contribution of PEG-4 can be treated as water in first approximation. Based on this approach, our 19.5 C data corresponds to a viscosity range of  $10^5 - 10^8$  Pas."

Referee #2: How do you account for changing solubility as the droplet composition changes in additional studies? Given your account for non-ideality as noted in point 5, does this treatment persist between each condensed shell?

Authors' response: As we are studying a Fickian diffusion process, which is driven by concentration gradients alone, during which our system neither phase separates nor partially effloresces, solubility is not an issue. The activity coefficient only influences the effective PEG-4 vapor pressure and therefore our model just requires treatment of the activity coefficient for the outermost shell. Consequently, in its current form, our model is not applicable to systems that undergo phase changes.

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Referee #2: It seems in section 4.1 that you optimize the activity coefficient, but how much error is inherent from other experimental sensitivities in this procedure? In other words, would it be possible to show the impact on inferred diffusion if you used a purely theoretical calculation of activity coefficients? It might be in more complex systems, unless you could use a robust multidimensional optimization strategy, this would be required anyway. I appreciate you discuss some of these issues in section 4.2 but the paper would benefit from a 'pure' sensitivity simulation.

Authors' response: In the non condensed-phase diffusion limited regime, which was used to determine the activity coefficients, the accuracy with which activity coefficients can be determined hinges on our knowledge of the pure component vapor pressure of PEG-4, which is better than  $\pm 10\%$  (95 % confidence interval) (Krieger et al., 2017). As pointed out by Referee #2, the sensitivity of the inferred diffusivities on activity coefficient was addressed in the y-error-bars given in Fig. 7 of section 4.2, for which the flux into the gas phase was multiplied or divided by a factor of 3. Below  $D_{PEG} < 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ , this treatment had no influence on the retrieved diffusivities and the error bar given in the figure reflects a conservative estimate that the error in manually fitting the slope is not bigger than a factor of 1.4. Above  $D_{PEG} \sim 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ , the error bars given in the figure are dominated by the multiplication/division of the flux into the gas phase by a factor of three. While we did not explicitly calculate the activity coefficients in each time step using theoretical calculations, the factor three that we applied widely exceeds the range given by AIOMFAC (see Fig. 5). In the condensed phase diffusion limited regime, the diffusivities are not very sensitive to the activity coefficient. We chose the RH range of our measurements conservatively in order to avoid strong sensitivity of diffusivity to activity coefficients. In this sense, only very small activity coefficients (of less than  $\sim 0.1$ ) are likely to bias inferred diffusivities. However, the activity coefficient measurements and AIOMFAC calculations both indicate values close to ideality and  $> 1$ .

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Referee #2: Could you please add more specific details on how you optimize your activity coefficient values? Is this done by a specific algorithm, set tolerance or by eye

Authors' response: The activity coefficients were optimized by eye. To address Referee # 2 comment, we will add the following sentences to the revised version of the manuscript: "We determine  $\gamma_{PEG}$  at high RH by freely adjusting its value in the diffusion model to reproduce the experimental radius curve presented in Fig. 4a (red) while  $D_{PEG}$  was set to a constant value of  $1.0 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ . **The best activity coefficient fit was determined by eye.** The chosen diffusivity is well within the gas phase diffusion limited regime ..."

Referee #2: On this note in section 4.2 the authors comment on the challenge in propagating errors in this model. With the availability of some algorithms to do this, it would be great to add a note on where others might be able to obtain the code to perform such calculations or how best to collaborate on this.

Authors' response: We will add the following sentence to the manuscript: "As the determination of  $D_{PEG}$  still requires knowledge of  $\gamma_{PEG}$ , we rely on Wilson's approach for multi-component systems (Orye and Prausnitz (1965)), Appendix A3) to parametrize  $\gamma_{PEG}$  based on binary and ternary bulk data as well as EDB  $\gamma_{PEG}$  measurements in the gas diffusion limited regime. **The code of our diffusion model is available upon request.**"

Referee #2: [on section 5] It begs the question how we might move towards more general quantification. Perhaps a useful addition is to ensure we start to study

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affects in ensemble populations through chamber and box-model studies. The impact on size distribution should also be studied

Authors' response: We agree with the reviewer, but these suggestions are beyond the scope of the present paper.

## References

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