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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Predictions of diffusion rates of organic molecules in secondary organic aerosols using the Stokes-Einstein and fractional Stokes-Einstein relations" *by* Erin Evoy et al.

Anonymous Referee #3

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The manuscript submitted to *Atmospheric Chemistry and Physics* titled "Predictions of diffusion rates of organic molecules in secondary organic aerosols using the Stokes-Einstein and fractional Stokes-Einstein relations" by Evoy et al. presents diffusion coefficients, D, and viscosity, η, of fluorescent dyes in organic compounds, which are proxies of secondary organic aerosol (SOA) material. Using their data and data from previous studies, they test the applicability of the Stokes-Einstein (SE) relation. The authors find that although the SE relation is fairly accurate within their experimental uncertainty, a better fit could be made using a fractional Stokes-Einstein (FSE) relationship, with 2 fit parameters to adjust the linear relationship between $\ln D$ versus $\ln \eta$. The authors compare the SE and FSE relation in terms of mixing times, τ, calculated

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Discussion paper

for particles 200 nm in diameter as a function of latitude and pressure levels in the atmosphere. The authors conclude that when η is high, τ and D calculated using the FSE are up to 10 times shorter.

Overall, this manuscript adds to the growing database of D and η for many atmospherically relevant compounds and proxies. The methods are accurate and the error analysis is justified. Finally, the results and implications are presented clearly. I will add that this manuscript was a pleasure to read and review. There is one major comment about how previous literature is described by the authors. A few minor comments must also be addressed before I can recommend publication. Page and line numbers are indicated below, and all references are taken from the manuscript.

Major comment

p. 2, l. 13-17: The authors use these sentences to claim importance of SOA growth, mass, chemical reactivity and photochemical reactivity. These statements are valid but for a limited range of conditions. The authors should state what range of D or η these are actually valid, or readers not in the field may be misled. Specific examples should be given here to reveal to the reader when diffusion limitations significantly affect atmospheric processes such as SOA growth or photochemical reactions and when they do not. This paragraph can be extended to discuss these details. I will only discuss a few references below, and implore the authors to recheck all cited previous publications here for the conditions of D and equilibrium timescales, τ, that are important for SOA formation and (photo)chemical reaction.

- Shiraiwa and Seinfeld (2012): Measurements in this manuscript are for $10^{-15} - 10^{-6}$ cm^2 s^{-1}. However, Shiraiwa and Seinfeld (2012) show that values of τ are unchanging when D is varied between about $10^{-15} - 10^{-5}$ cm^2 s^{-1}. This says to me that changes in D are not important at all to τ for their observations, and thus not important to SOA growth. It can be important for a lower range of D and a specific particle size, however these details are not included in the manuscript.

This should change in the introduction.

- Zaveri et al. (2018): In Figs. 4 and 5 of Zaveri et al. (2018), size changes for SOA particles ≥ 200 nm in diameter could be successfully modeled using both liquid-like and semi-solid scenarios. This would lead to the conclusion that, changing D and τ for 200 nm particles shown in Fig. 5 of this submitted manuscript would not make any difference to SOA size or mass. This is contrary to what they write.
- Hinks et al. (2016): How does viscosity change light absorption and quantum yield of a photochemical reaction rate? Excitation reaction R1 in Hinks et al. (2016) is not altered by changing D. Therefore, the statement that "photochemistry" depends on D is incorrect. However, chemical reactions R2-R4 could be diffusion limited. These details should be stated, otherwise this statement can mislead readers.

Minor Comments

1. p. 1, l. 20-21: The authors did not measure D. They measured the change in florescence intensity over time. D was derived from fitting their florescence intensity measurements, and then fitting again their fitted parameter ($r^2 + 4Dt$) over time (p. 6, l. 9 and 15). Please search for all instances of the phrase "measured diffusion coefficients" or similar and rephrase.
2. p. 1, l. 27-28: The authors make the claim that differences in D between the SE and FSE relation can be important for predicting SOA particle size and chemical reaction rates. SOA size or reaction rates were not measured or modeled in this manuscript and so this sentence misleads readers. This is more of an introductory sentence than a consequence determined by their results. This sentence should be included in the beginning of the abstract and reworded for clarity.

3. p. 1, l. 28-29: This sentence is a very unusual way to end an abstract. What I read here is that the diffusion results are important when diffusion is important. This is a very weak sentence and suffers circular reasoning. Please rephrase.
4. p. 6. l. 8 and Equation 2: I am confused about how the fitting was done, likely because of Fig. S6. Was a time evolving surface fit (2-D) performed? Was the data first averaged as in Fig. S6, and then fit in 1-D? Please briefly clarify what was actually fit in the text.
5. Figure S6: I question why averaging over the y-direction was used here. The corners of the bleached rectangle should “round” as time progresses (Fig. S4e), and the spot then appears more like a circle. Therefore, can averaging over the y-direction really be called a cross-section? Would the authors agree that showing a measured 2-D surface intensity plot and modeled lines of constant intensity would be more beneficial to understand the measurements and fit?
6. p. 8, l. 17-18: I am pleased that the authors have not oversold themselves here and used words like “suggest” and “may”. Throughout their manuscript, their data and analysis has been worded very well.
7. p. 9, l. 1-3: Is this too obvious? More fitting parameters will always give a better fit. Is a quantitative metric to evaluate whether or not the data are consistent with a certain model? As it is written, the authors want the reader to look at the residuals in Fig. 3b) and c) and come to the same qualitative reasoning. I would recommend a simple chi-squared test to give quantitative evidence and strengthen their claim.
8. Figure 3a and Eqn 3: When the authors fit to the FSE relation, did they consider a weighted fit to the uncertainties? I could imagine some data points by different authors are more certain than others. Please state in the manuscript if the fit was weighted with any uncertainties.

9. From the journal website, “Authors are required to provide a statement on how their underlying research data can be accessed. This must be placed as the section “Data availability” at the end of the manuscript before the acknowledgements.” Please fulfill this data policy requirement.

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