

Review for “Viscosity of aqueous ammonium nitrate–organic particles: Equilibrium partitioning may be a reasonable assumption for most tropospheric conditions” by Klein et al.

Klein et al. measured the viscosity of particles with internally mixed NH_4NO_3 and sucrose using three techniques at atmospherically relevant humidity. The authors then predicted the viscosity based on mixing rules and the AIOMFAC-VISC model. They found that the mixing rule based on mole fractions is sufficient to predict the viscosity of a ternary system, e.g., the internally mixed NH_4NO_3 , sucrose and H_2O . As viscosity is a very important property of aerosols and the observation data showing how the viscosity changes with particle composition (e.g, mixed inorganics and organics) are still very limited, this study is helpful in understanding the viscosity of internally mixed particles. However, I have some concerns about the authors’ understanding of gas-particle partitioning. I recommend the publication of this study after the following comments could be addressed.

Major comments:

- (1) My major comment arises from that the authors may have mixed the definition of mixing time and equilibrium time. Mixing time and equilibrium time are two different time scales. The equilibrium time refers to the time scale to achieve gas-particle equilibrium, affected by many factors, including particle viscosity, the volatility of partitioning compounds, particle size and concentrations etc, as gas-particle partitioning is controlled by gas-phase diffusion, interfacial transport, and particle-phase diffusion (Mai et al., 2015; Shiraiwa and Seinfeld, 2012; Li and Shiraiwa, 2019). However, the mixing timescale is mainly related to the particle-phase diffusion, as the authors wrote in Equation (2) in this study. Therefore, I suggest the authors be careful when using the term of “equilibrium time”, e.g., the section of Appendix C, where the equilibration times are actually mixing timescales (Line 603, Line 616-619, Table C1).
- (2) The authors applied three mixing rules, i.e., the mole-fraction based, the mass fraction based, and ZSR, to predict viscosity of the NH_4NO_3 -sucrose- H_2O system. Many other studies also applied the Gordon-Taylor equation combined with the VTF equation to predict the viscosity of particles with mixed compounds (Dette and Koop, 2015; Li et al., 2020; O'brien et al., 2021; Koop et al., 2011). As the values of T_g of NH_4NO_3 , sucrose, and H_2O are available, it is possible to estimate the viscosity based on the Gordon-Taylor equation. Would the predictions using the Gordon-Taylor equation agree with the predictions based on the mole-fraction based mixing rule?
- (3) In the section of 3.3 for Atmospheric Implications, the authors stated that “global models often assume equilibrium partitioning is achieved for fine particulate matter... if the mixing times exceed the chemical time step, it makes the quasi-instantaneous equilibrium assumption questionable”. I do not agree with

this statement. Note that current chemical transport models (CTMs) often assume SOA partitioning is rapid, i.e., instantaneous equilibrium partitioning (Pankow, 1994) is usually employed for the gas-particle partitioning of semi-volatile organic compounds (SVOCs) forming SOA particles. When particle is viscous, however, the equilibrium timescale of SVOCs can be longer than 1 h, in which case kinetic partitioning of SVOCs should be considered instead of instantaneous equilibrium partitioning (Li and Shiraiwa, 2019; Maclean et al., 2021; Zhang et al., 2024). For NH_4NO_3 partitioning, however, I think there is no argument questioning the assumption of instantaneous equilibrium of NH_4NO_3 partitioning currently applied in CTMs. Therefore, I am wondering the meaningfulness of calculating the mixing timescales of NH_4NO_3 partitioning in fine particles. In the abstract, the authors should clearly state that they actually calculated the mixing time of NH_4NO_3 in internally mixed particles and in the paper title, the authors should clarify that equilibrium partitioning may be a reasonable assumption for NH_4NO_3 partitioning. In addition, at Line 314, the authors wrote “the mixing time scales with the square of the particle radius, regardless of the composition”. This is not correct as the mixing timescales do relate to the composition because the bulk diffusion coefficients are different for different diffusing compounds.

Specific comments:

- (1) Line 90: I could not find the SI file attached?
- (2) In the caption of Figure 3, is Tong et al. 2018 actually Tong et al. 2022?
- (3) Line 251-253, the authors concluded that the viscosity values reported in Tong et al. (2022) for $\text{NH}_4\text{NO}_3\text{-H}_2\text{O}$ (Fig. 4) are questionable due to the volatilization of NH_4NO_3 . Does this mean their data for the pure NH_4NO_3 showed in Fig. 3A are also questionable? Their data look comparable to Laliberté (2007) in Fig. 3A.
- (4) Line 258, in your system, what is the possible reason for the significant increase in viscosity below a_w of 0.1?
- (5) Line 315-316, the authors calculated the diffusion coefficients of NH_4NO_3 via the Stokes-Einstein relation. However, previous studies have showed that the Stokes-Einstein relation is not suitable (with large underestimation) to predict the diffusion coefficients for such small diffusing molecules (Evoy et al., 2020; Price et al., 2015). Please also double check the calculation of $D_{\text{H}_2\text{O}}$ (Line 613) in Equation (C1).
- (6) Line 200: “ 10^{12} Pa” should be “ 10^{12} Pa s”.
- (7) Caption of Figure 6: “the viscosities of $\text{NO}_3\text{-sucrose-H}_2\text{O}$ ” should be “ $\text{NaNO}_3\text{-sucrose-H}_2\text{O}$ ”.
- (8) Table A1, what temperature the viscosity parameterization showed in Table A1 is suitable to?
- (9) The mixing times showed in Fig. B2 are for which compound? The mixing times of different molecules are very different (refer to my major comment 3).
- (10) Table C2, what d_{max} is? Is it the diameter of film?

References

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