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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Discontinuities in hygroscopic growth below and above water saturation for laboratory surrogates of oligomers in organic atmospheric aerosols" *by* Natasha Hodas et al.

Anonymous Referee #1

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Hodas et al. present data on hygroscopic growth and CCN activation for PEG of different molecular weights and PEG particles mixed with AS. These data are analyzed in the context of a modified version AIOMFAC for equilibrium water uptake and a viscosity/diffusion model for kinetic limitations due to diffusion. The models are used to conclude the extent to which viscosity contributes to differences in water-uptake behavior below and above water saturation that are reported in the literature.

This manuscript touches on a range of important issues that are currently debated in the literature. In general, it captures the gist of these discussions well. With appropriate revision, the manuscript is in principle publishable in Atmospheric Chemistry and Physics.

However, in it’s present form, the manuscript isn’t a strong contribution. The ideas revolving around viscosity are interesting and new and the assumptions made to model potential effects are quite reasonable. In contrast, the data analysis, and theoretical discussion could be significantly improved. Throughout the manuscript, various claims about agreement of the measurements with prior work and the effect of surface tension effects on CCN are not sufficiently backed up.

Major comments:

(1) The PEG water uptake measurements should be compared to bulk water activity data before using modified AIOMFAC. The data are readily available (e.g. Gaube, 1993). While AIOMFAC has it’s place to interpolate activity coefficients it is more a test of how well activity coefficient models can reproduce data and less a test if the measured DASH-SP data are consistent with bulk water activity data.

(2) The CCN data analysis should be improved.

- The fits to the data in Fig. 2 are poor. For example, the black lines don’t seem to go through the data at all. Even the AS control fit seems to off by a few nm, which will strongly influence the calibrated supersaturation. Issues to be addressed include: application of multiple charge correction for DMA transfer, application of loss correction in the CCN, which explains the gradual trend from 0.8 to 1 activated fraction in the plot, and application of a more appropriate fit function to better represent the data.

- Include the relationship between AS and dry diameter and sc that is assumed in the calibration. Is it possible that the calibration drifted between measurements?

- State whether or not there is an accounting for particle shape effects in the comparison with AS. How would that affect your conclusion since PEG is liquid and spherical in comparison.

(3) Improved CCN theoretical analysis is needed. The manuscript states that “observed increases in CCN activity with molecular mass and the enhancement in the CCN activity of PEG10000-AS compared to pure AS can likely be attributed to the fact that PEG is surface active and has been shown to lower the surface tension of the air-water interface when present in aqueous solution.”. To date all experiments of mixtures of inorganic + organic surfactant have shown that the CCN activity of mixed particles is less than than what would predict even from ZSR (Prisle et al., 2010, Petters and Kreidenweis, 2013 and Petters and Petters, 2016). In other words, the data unanimously show that dissolved surfactants suppress CCN activity. These results are broadly supported by CCN theory that includes appropriate water activity and surface tension treatment in Kohler theory, although it should be understood that those descriptions still require further development. Nonetheless, the reported enhanced CCN activity of PEG10000-AS compared to pure AS is an extraordinary conclusion that requires significant elaboration. To support this finding a revised paper should include

- improved data analysis (see point 2).

- discussion of experimental issues raised in Petters and Petters (2016), which include fractionation of composition in the atomizer and serious questions regarding reproducibility of CCN measurements for surfactant aerosols. While it may well not be an issue for the particular system used here, a single CCN data point using a similar methodology is insufficient to support the claims made.

- quantitative comparison of pure PEG CCN data, including those in Petters et al. (2009) for PEG 200, 450, and 2000. Their data follow the decreasing trend one would expect with increasing molecular size from theory. It would be important to demonstrate whether or not the data agree at lower MW and how much the trend of decreasing CCN with MW reverses for the higher MWs. (Quantitative agreement between the datasets is not a necessary condition for publication; however, the reversal from a theoretically expected trend requires quantification and discussion about potential reasons for the behavior).

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- quantitative surface tension data to support the stated increase in surface tension with molecular weight.

- accurate description of water activity at RH near activation, with uncertainty fits based on DASH-SP, bulk water activity data, and/or AIOMFAC.

- theoretical CCN predictions using water activity and surface tension using the available data and the authors choice of any of the widely available descriptions of CCN theory including surfactants (Sorjamaa et al., 2004, Raatikainen and Laaksonen, 2011, Topping, 2011, Petters and Kreidenweis, 2013, Ruehl et al., 2016). If satisfying closure between different measurements and measurement and theoretical predictions cannot be achieved, the conclusions in the paper should reflect those uncertainties.

"After entering the DASH-SP inlet, the aerosols are further dried in a Nafion dryer (with a residence time of 1 s), they pass through a 210 Po neutralizer, and are then size-selected with a long-column differential mobility analyzer (DMA) based on their electrical mobility"

- what was the RH? Can residual water affect the measurement?

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