Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2016-236-RC1, 2016

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 #2

Received and published: 16 May 2016

Summary:

This paper presents hygroscopic growth factors (HGFs) and cloud condensation nuclei (CCN) activity of particles composed of ammonium sulfate and/or polyethylene glycol (PEG) polymers (MW = 200, 1000, or 10000 g/mol). This data is used with a water activity model to conclude that kinetic limitations to water uptake are negligible, and that differences in water uptake under sub- and supersaturated conditions are caused by “a combination of RH-dependent differences in the sensitivity of water uptake behavior to non-ideal interactions and to surface tension effects.” This topic is of interest to

ACP readers, and both the data presented and the analyses are sound. I recommend publication once the comments below have been addressed.

General Comments:

In the abstract, one of the main conclusions (quoted above) regards “apparent discontinuities in hygroscopicity above and below water saturation.” Two paragraphs in the introduction discuss “previous studies [that] have observed low degrees of hygroscopic growth below water saturation, but high CCN activity.” Although the authors emphasize the fact that PEG10000-AS particles are more CCN active than pure AS, they do not explicitly conclude that PEG hygroscopicity is greater under supersaturated (CCN) conditions than it is under subsaturated (HGF) conditions. Instead the focus is shifted to MW dependence, and I wasn’t sure whether the authors thought it was obvious that the “gap” in hygroscopicity was present, or that it was outside the scope of this work. I recommend the authors present data that would allow the difference in PEG hygroscopicity under sub- and supersaturated conditions to be evaluated. For example, CCN activity data is compared to pure AS, and this could also be done for HGFs. Or, a single hygroscopicity parameter that accounts for differences in RH and particle size could be reported for both situations.

In general the influence of water activity (the Raoult effect) on hygroscopicity is thoroughly addressed. The same cannot be said for surface tension (Kevin) explanations, however, despite the fact that this is the explanation given for a key observation in the abstract (lines 32–34): "[A]n increase in CCN activity with increasing PEG molecular mass was observed. This . . . is attributed to an increase in the efficiency of PEG as a surfactant with increasing molecular mass." There are instances where the surface activity of PEG200, PEG1000, and PEG10000 are compared, but the specifics of the comparison are not clear (see Specific Comments). Also, no attempt is made to quantify these differences in surface activity. The authors could model CCN activity accounting for surface-bulk partitioning of PEG using the Szyszkowski equation or some other equation of state. Alternatively, a simple single-parameter approach could be used. If the CCN activity of the PEG is believed to arise from its surface activity, it could be parameterized as δorg, which is the thickness of the organic film at activation assuming all organic material is adsorbed to the surface (Ruehl et al., 2016). At a supersaturation of 0.6%, Dcrit of 53, 47, and 34 nm are reported for particles with a 1:2 mass ratio of ammonium sulfate to PEG200, PEG1000, and PEG10000, respectively. This is equivalent to δorg of 0.19, 0.12, and 0.04 nm. For linear carboxylic diacids with carbon numbers from 3 to 8, Ruehl et al. (2016) found that δorg ranged from 0.07 to 0.21 nm. The similarities in these ranges of assumed film thickness support the conclusion that PEG primarily contributes to CCN activity of mixed inorganic-organic particles through its surface activity.

The conclusion that the results reflect “RH-dependent differences in the sensitivity of water uptake behavior to non-ideal interactions” (lines 39–40 of the Abstract) should be made more clear. If the “RH-dependent differences” are between sub- and supersaturated conditions, then the conclusion is that non-ideal interactions are important at RH$\leq$90% and negligible at RH$\sim$100%. But doesn’t this simply arise from the convention of setting the activity coefficient to unity at infinite dilution? Or, are the authors actually taking about “MW-dependent” differences? Figure 7 suggests that water activity models need to take molecular size into account, because Raoult’s law will underpredict water uptake for high-MW compounds. I am not sure that the authors can conclude anything more general than this.

Specific:

Page 12, line 14 – what is meant by the “magnitude of this surface tension depression” – does this mean the minimum surface tension value possible? Or does it refer to the relationship between surface tension and concentration (e.g., a Szyszkowski parameterization)? If it has been established that PEG surface activity increases with MW, is it known that this relationship holds at the high values of water activity relevant for CCN activation? The textbook cited (Rey and May) does not provide much guidance – it might be better to cite a relevant paper from the textbook bibliography.

Page 14, line 9 – could you provide a brief explanation for why LLPS decreases water uptake? Is this always true, or just for the particle sizes and compositions in this work?

Page 14, line 29 – while I understand that the diffusivity of water in pure PEG is too fast to account for the “hygroscopicity gap”, I wonder if this is relevant at all for particle hydration. Wouldn’t PEG particles dissolve from the outside inward when exposed to increasing RH? And so wouldn’t the diffusion of water through a (non-supersaturated) PEG aqueous solution be more relevant than through pure PEG? Note that this is different from drying a particle from the outside – in that case, a viscous supersaturated PEG “shell” would form, and any water in the droplet interior would have to diffuse through this shell before equilibrium could be reached.

Page 16, line 10 – what is meant by the “efficiency with which PEG depresses surface tension”? Is this based on the minimum value of surface tension possible? Or the magnitude of the reduction relative to PEG concentration? If the later, is this surface, bulk, or total concentration? Again, a better citation would help make this more clear.

Figure 3 – I recommend adding AIOMFAC predictions to this figure as well, or simply add predictions assuming an ideal solution. This will help put these data into context.

Citations:

Ruehl, C; Davies, J; Wilson, K: An interfacial mechanism for cloud droplet formation on organic aerosols, Science 6280, 1447-1450 (2016).

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-236, 2016.