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Atmospheric
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Discussions

Interactive comment on "Modelling the cloud condensation nucleus activity of organic acids" *by* Z. Varga et al.

Anonymous Referee #3

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The focus of this paper is to demonstrate the utility of direct osmolality measurements of aqueous organic solutions in determination of composition-dependent solution water activities. The authors also measure the composition-dependent solution surface tensions. By using these measured water activities and surface tensions in the equilibrium equation that expresses the conditions for ambient water partial pressure - drop partial pressure equilibria (their equation 1), the critical superaturations for selected dry particle sizes of the pure compounds can be computed and compared with existing laboratory data.

The use of the direct measurements of surface tension and osmolality is quite interesting. In particular, the authors show that the osmolality can be determined experimentally to very dilute conditions, which helps greatly to fill in the range of composi-

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tions currently accessible via other techniques, particularly HTDMA and EDB, which are restricted to water activities $< 95\%$. It would be terrific to apply this technique more broadly to both other under-studied pure components and to aqueous solutions formed from sampled atmospheric aerosols. It would also be quite interesting to see how other approximations approach these data (see note below), and for which conditions the errors introduced by such approximations are large enough to significantly affect CCN calculations.

I recommend this paper be published in ACP after consideration of the following points. Also, all of the Excel plots should be improved for ACP publication.

1. The use of equation (2) to discuss the relationship between water activity and the terms in the van't Hoff factor is not necessary, since one can show directly how water activity is expressed in terms of the van't Hoff factor (Kreidenweis et al., ACP, 2005, equation (7)). The discussion of the van't Hoff factor might also benefit from pointing out that $i \sim \nu\Phi$ (also shown in Kreidenweis et al., ACP, 2005). It can be seen that i represents both the number of moles in solution and nonideal solution behavior, and is a function of composition. Using a van't Hoff factor of unity thus assumes not only that the solute dissociates only weakly but also that its nonideal behavior - at least at the dilute conditions at which activation occurs - can be ignored (p. 3, bottom half of page, and elsewhere).

2. p. 4, top of page: it is pointed out that since dissociation constants are not known for atmospheric samples, variable van't Hoff factors cannot be computed. However, the molecular weights of the solute(s) are also not known, and therefore any use of the Kohler parameter "B" that involves estimating individual terms for unknown compositions is problematic. As has been suggested in several recent papers, another approach is to lump all solute-dependent parameters in "B" into a single unknown, the value of which should vary with composition but may be well approximated by a single value (this remains to be fully demonstrated for "real" aerosols, however).

3. In equation (1) [and in the A and B terms], ρ is not the density of the droplet solution. It is the density of pure water. The derivation of equation (1) yields the partial molar volume of water in the numerator of the exponential term, which can then be approximated by the molar volume of pure water, M_w/ρ_w.

4. p. 5, last paragraph: how is it evaluated what value of surface tension depression is "negligible"? Also, the composition of the solution at the point of activation should depend on whether the dry size is large or small. Small particles, although activating at a higher critical supersaturation, are much less dilute at the activation point. Thus one might expect to see more impact of surface tension depression for smaller dry particle sizes. This can be shown more clearly on a Sc-Ddry log-log plot (see points 6 and 9).

5. p. 6: The discussion of compound-to-compound variations, while correct, misses pointing out the following. The water activity expression underlying equation (2) is based on a corrected Raoult's law, which is in turn based on the mole fraction of water in solution. Therefore if expressed on a molar basis, every organic for which $i \sim 1$ is a good approximation will have the same impact on water activity and thus on activation. In other words, if the x-axis in figure 2 were changed to mole fraction, most of these lines would lie exactly on top of each other. This might be worth showing. Anyway, unless this is pointed out, it seems a bit misleading to indicate that the length of the carbon chain, for instance, has a strong effect on water activity, although it is certainly true that as components in real aerosols, variations in molecular weight and dry density would certainly lead to different Sc-dry diameter relationships.

6. Figure 4, figure 6 and figure 7: First, all the critical supersaturation - dry diameter plots would benefit from using a log-log scale. The theory and the data should approximate straight lines and I think such a presentation would be more clear. For these particular plots, extensive comparisons between the same published data referenced here and in some cases including one or two other published data series are found in Koehler et al., ACP, 2005. Although this paper is referenced it seems that some of the comparisons and findings did not make it into this manuscript. Koehler et al. also

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discuss the possibility that oxalic acid dihydrate is formed in lab experiments and show how this might affect measured GFs.

7. Figure 2: it is really interesting to show water activity as a function of wet-to-dry diameter. Of course this variable is simply the diameter growth factor (GF) measured in HTDMA studies. It would be interesting to show how the points here compare with HTDMA data which end at water activities below those accessible via osmolality. By combining the data sets, it should be possible to derive an expression for the water activity over the full range.

8. Solubility issues: It is pointed out that solubility limitations mean that for some compounds, the minimum water activity is actually quite high. Several points need to be made about this. First, the EDB and HTDMA might measure some metastable solutions at lower RH, and such data could be combined with the osmolality data. Second, if the initial particle is truly dry, activation may require high superaturations to overcome the deliquescence barrier (see the excellent discussions in Hori et al., JAS, 2003 and Bilde and Svenningsson, Tellus, 2004). I don't think any of the calculations shown reflect this phenomenon.

9. The effects of measuring composition-dependent i and surface tension on the estimated critical supersaturation are not really clearly identified here. It would be helpful to have a plot showing the estimated Sc-Ddry relationship for the assumptions of pure water surface tension and $i = 1$, and comparing with the more precise calculations. At least for comparison with lab data (Figures 6 and 7), it should be shown whether the osmolality and surface tension measurements significantly improve the theory-data comparisons or not. In general, although surface tension can be lowered by these compounds, one has to look at the value of surface tension for compositions near the critical point and evaluate how much suppression occurs there. Otherwise the shape of the approach to the critical point may vary, but the actual critical supersaturation may be little affected. This could be shown by drawing the respective Kohler curves, for an assumed compound and dry size, under both sets of assumptions regarding the solution

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behavior and showing where the curves differ.

Minor points:

Sun and Ariya reference is missing.

Shulman reference is out of order.

What is the methodology for computing the van’t Hoff factor from the osmolality data?

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