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Atmospheric
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Discussions

Interactive comment on “Increased cloud activation potential of secondary organic aerosol for atmospheric mass loadings” *by* S. M. King et al.

S. M. King et al.

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We appreciate the reviewer’s comments and the resulting improvements to the manuscript. Reviewer comments are in bold. Author responses are in plain text. Modifications to the manuscript are in italics.

This manuscript discusses the CCN activity of secondary organic aerosol generated via ozonolysis of a-pinene in the presence of an OH scavenger. The experiments were conducted using quasi-monodisperse ammonium sulfate seed aerosol and data are presented for various organic aerosol mass loadings in the chamber. Because the chamber was operated in continuous flow mode the resulting aerosol size distribution and size-dependent mixing state is complicated.

A detailed microphysical model is used to fit the resulting complex activation curves. Using this model in conjunction with two-component Kohler theory the authors infer the effective hygroscopicity of the organic component as a function of aerosol mass loading. The observed increase in effective organic aerosol hygroscopicity is then interpreted as a 10% reduction in solution surface tension. The authors suggest that the surface active compounds have low volatility and thus are more abundant, on a relative basis, at low organic aerosol mass loadings.

The paper is well written and I recommend that this manuscript will be published in Atmospheric Chemistry and Physics.

Minor comments: In the model used by the authors it is assumed that the effective organic hygroscopicity of the pure compound equals the expressed organic hygroscopicity in the mixture, i.e. there are no organic-inorganic interactions. So far only the work of King et al. (2007) can be used to substantiate this assertion. My question is: the low volatility compounds, which are currently asserted to be surface active, might also behave nonideally in other respects. For example they might be chemically reactive or interact with the ammonium or sulfate ions in solution. If so, the surface tension lowering is only apparent.

The reviewer's discussion on other possible nonidealities of the system is relevant and correct. We agree with the comments, and have added text as follows to clarify this point (pg. 1685, lines 23+):

"The sensitivity to another possibility, namely a 10% increase in the van't Hoff factor i_{ORG} *at lower loadings (e.g., resulting from an increase in the relative fraction of carboxylic acids, which dissociate, or from nonidealities introduced by interactions between the organic and the inorganic components), is approximately equivalent to that of a 25% decrease in* $V_{m,\mathrm{ORG}}$ *(King et al., 2007). Combined changes within the*

particle can also be more complex than represented in our model. For example, the possible partitioning of more surface-active molecules from the droplet interior to the surface layer can change the droplet composition sufficiently to increase the water activity, thereby counteracting the effect of surface tension reduction (Sorjamaa et al., 2004; Prisle et al., 2008). This kind of possibility is not explicitly considered in our analysis."

Similarly, increases in organic aerosol acidity or decreases in molecular weight can lead to equivalent increases in apparent organic aerosol hygroscopicity, which might be mistaken for a surface tension effect. Given that carboxylic groups are most effective in lowering the vapor pressure of organic compounds it seems plausible to me that carboxylic acids are more abundant at low mass loadings. This is also consistent with the increase in m/z=44 fraction observed by the AMS.

The reviewer makes a good point, and the following modifications have been made regarding the probable increase in carboxylic acids:

[Page 1685, lines 5+]: "Signal at *m/z* 44 includes fragments of oxo- and di-carboxylic acids, and the increase for lower organic mass loadings plausibly indicates a corresponding increase in the mass fraction of these oxygenated, polar compounds, representing the types of organic molecules normally considered CCN active. Possible causes for the increase in oxygenated fraction at low loadings are discussed in Shilling et al. (2009). *Notably, Capouet and Müller (2006) report that the volatility of carboxylic acids may be amongst the lowest of all the products of* α*-pinene ozonolysis."*

[Page 1686, end of text]: *Other factors, such as decreased molecular weight, increased density, or increased van't Hoff factor, can contribute to the explanation but*

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are quantitatively insufficient as the full explanation. As a hypothesis, an enrichment of carboxylic acids at low loadings, as suggested by Capouet and Müller (2006) and as consistent with the mass spectra reported by Shilling et al. (2009) for these experiments, anticipates a decrease in surface tension because carboxylic acids have been shown to reduce surface tension (Shulman et al., 1996; Hyvärinen et al., 2006; Topping et al., 2007; Tuckermann, 2007)."

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 1669, 2009.

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