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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Inferring thermodynamic properties from CCN activation experiments: a) single-component and binary aerosols" *by* L. T. Padró et al.

L. T. Padró et al.

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Reply to Reviewer # 3

General comment:

The authors present a new method, Köhler Theory Analysis (KTA), for inferring molar volume and solubility of organic compounds in single component and binary organic-ammonium sulfate aerosols. Application of the theory relies on measurements of droplet surface tension, . . . low organic mole fractions.

This work is an important step toward characterizing the influence of organic constituents on the cloud droplet formation potential of ambient atmospheric

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aerosols and related climate change effects. It should be of significant interest for readers of Atmospheric Chemistry and Physics. The manuscript is well-organized and well-written, with sufficient detail of the theory, assumptions, formulas, notation, experimental methods, and calculations.

However, the general conclusion that the KTA method is a "...powerful tool for characterizing the droplet formation potential of ambient water soluble organic carbon..." is an overstatement. Typical ambient atmospheric aerosols can range in chemical composition from primarily inorganic to primarily organic, and may contain numerous individual organic and inorganic components. While useful and informative, the KTA method had reasonable success for only single-component and binary organic-inorganic solutions with high organic mole fractions. Substantial errors were reported for more general aerosol mixtures having equal mole fractions of organic and inorganic components.

True, errors increase together with the amount of inorganic (in fact, it scales inversely with organic volume fraction), but we do not agree that KTA would work well only for very limited aerosol systems for the following reasons:

1. Departures from Köhler theory are often strongest for binary organic-inorganic mixtures. In complex water-soluble organic mixtures (where the mol fractions of individual compounds are small) the entropy of mixing tends to dominate the free energy term (vs. the energy interactions) and forces the solutions to behave much more "smoothly" (i.e., ideally). KTA would then describe the "average" properties of dissolved organic quite effectively, and for a larger dynamic range of organic mol fractions.

2. Even for the extreme case of a binary mixture, good agreement with expected molar values is obtained for an organic fraction of 50% and above. This covers a rather large range of atmospheric aerosol.

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3. When the organic fraction is less than 50%, once can still obtain a molecular weight (which is just subject to larger uncertainty). Under such conditions, organics would have a small impact on CCN activity, hence larger uncertainty in molecular weight do not translate to large uncertainty in CCN activity and number.

Given that we have already applied KTA to ambient aerosol with reasonable success (e.g., in characterizing the water-soluble fraction of biomass burning aerosol, Asa-Awuku et al., ACPD; secondary organic aerosol from alkene ozonolysis, Asa-Awuku et al., ACPD) we stand by our statement that KTA is "a potentially powerful tool" to characterize the water-soluble fraction of ambient aerosol.

Specific Comments

Abstract and Conclusions: In the Abstract, the method is stated to infer molar volumes "...within 18% of their expected value for organic fractions between 90 and 100%." In fact, the 18% error value is an average, and not an upper limit. The statement should be changed to indicate this fact. In the Conclusions section, a similar statement is made, but there the range of organic fractions corresponding to the 18% error value is stated to be 50 to 100%. It is not clear why the stated ranges of organic mole fractions differ between the Abstract and Conclusions section.

We have made corrections in the organic range in the abstract and conclusion. We also have state that 18% is an average value.

Table 2: The temperature(s) corresponding to the chemical properties listed in Table 2 should be indicated.

The temperature for the solubility and pKa data are not always specified, and not included for this reason. Since the data is used in a qualitative sense (i.e., just for "ranking" the compounds), we feel this is not a major issue.

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p. 3810, line 10: It would be helpful if the authors justified the values chosen for the van't Hoff factors for the compounds studied in this work, perhaps by reference to other work.

In agreement with other laboratory studies (e.g., Cruz and Pandis, 1997; Raymond and Pandis, 2002; Broekhuizen et al., 2004; Abbatt et al., 2005; Hartz et al., 2006) the value of the van't Hoff factor for the organics used was chosen to be equal to 1 due to their low dissociation in water for typical atmospheric conditions. References have also been added for the effective van't Hoff factor for ammonium sulfate (e.g., Brechtel and Kreidenweis, 2000).

p. 3819, line 18: It is unclear and confusing as to why van't Hoff factors equal to 1 were used for the organic compounds studied when the authors state here that the values are larger in reality.

The van't Hoff factor may be slightly larger than unity (not by much for the compounds studied here) but we wanted to explore the impact of having it set to unity, as that would be the approach used when applied to ambient aerosol.

Table 5: It would be helpful if the authors provided some interpretation of the large variation in inferred molar volume errors and uncertainties across the organic compounds

studied.

Done. Discussion provided in section 4.3 of the revised manuscript.

Technical Comments:

p. 3810, line 10: Should read "...(for which a value of..." – addition of "for"

Done.

p. 3811, line 12: Add a comma after close parenthesis.

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Done.

p. 3812, line 4: Should read "...for Eq. (10) are obtained..." - substitution of "are" for "is"

Correction has been made in the manuscript.

p. 3817, line 11: Should read "...and organic molecules..." - not "...and organics molecules..."

Correction has been made in the manuscript.

p. 3817, line 19: Add a comma after close parenthesis.

Done.

p. 3818, line 8: Should read "...most compounds studied are not strong..." - addition of

"studied"

Correction has been made in the manuscript.

p. 3820, line 12-13: The statement, "The estimated molar volume error was found to

be larger than reality" is confusing. Suggest rewording for clarity.

Done.

Figure 6, Caption: Should read "Activation curves..." rather than "Activation curve..."

Done.

Figure 7: It would be helpful if the ranges of the ordinate axes in Figures 7a and 7b were equal.

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Good point. Done.

References:

Abbatt, J. P. D., Broekhuizen, K. and Kumar, P. P.: Cloud condensation nucleus activity of internally mixed ammonium sulfate/organic acid aerosol particles, Atmos. Environ., 39(26), 4767-4778,2005.

Asa-Awuku, A., Nenes, A., Sullivan, A. P., Hennigan, C. and Weber, R. J.: Investigation of Molar Volume and Surfactant Characteristics of Water-Soluble Organic Compounds in Biomass Burning Aerosol Atmos. Chem. Phys.,in review.

Broekhuizen, K., Kumar, P. P. and Abbatt, J. P. D.: Partially soluble organics as cloud condensation nuclei: Role of trace soluble and surface active species, Geophys. Res. Lett., 31(1), Art. No. L01107, doi: 10.1029/2003GL018203,2004.

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Interactive comment on Atmos. Chem. Phys. Discuss., 7, 3805, 2007.