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Atmospheric
Chemistry
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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 # 1

General comment:

The authors have presented a new technique (Kohler Theory Analysis, KTA) to infer thermodynamic quantities from CCN experiments. This method has been tested for single-component and binary aerosols with moderate success but continues to show substantial errors. Even with these errors, this tool is clearly and important step in better obtaining information from real and complex aerosol particles in order to better constrain models. The paper is clearly written and the method well-explained and analyzed for error. The importance and conclusion,

however, are overstated in light of the limited and mixed results obtained from this one study. This paper is an important early step in working to better understand organic aerosols and improving their modeling; it should be of interest to the readers of ACP.

We thank the reviewer for their thoughtful and critical review. This is the first of many studies that will characterize and develop KTA. Including this paper, there are 3 KTA papers in ACP (more to appear in the near future); in the other manuscripts, KTA is applied to much more complex ambient aerosol; our conclusions are in part reflecting the encouraging results obtained for all KTA applications to date. The concerns with regard to the method uncertainties are well taken and we have modified the characterization of KTA as “a potentially powerful tool”, to accommodate the reviewer’s concerns.

Specific comments:

The conclusion that KTA predicts “molar volume to within 18% of expected value” (P3820 L10) is misleading. Only the average of the high organic fractions come to 18% - individual errors were reported up to 83% for Azelaic Acid. Total Uncertainty (Table 6) actually averages to 51% for these same mixtures.

Our conclusion is not misleading, as it reflects what the data is telling us: estimation of molar volume using data from one supersaturation could yield large errors, but averaging over many supersaturations substantially reduces the error (to the stated 18%) as the effects of variable surface tension, surfactant partitioning, van’t Hoff factor, experimental uncertainty, etc. largely cancel out. Table 6 presents an *estimate* of the uncertainty in molar volume, which is shown to overestimate the real (average) error in inferred molar volume. These points have been clarified in the text.

The authors could make the statement clearer by writing: “Köhler theory analysis was found to predict the molar volume to within 18% of expected value for high organic mass fractions ranging between 50% and 100%.

Done.

While total uncertainty increases with decreasing organic content (Table 6), the pattern for Molar Volume error (Table 5) is much less clear and should be explained. For instance, Succinic Acid error first decreases and then increases for decreasing organic fraction while Azelaic Acid shows no pattern at all.

We have included a discussion for the pattern for molar volume error in Section 4.3. Two types of patters are seen in the data: $i)$ for the soluble non-surfactants (fructose, malonic acid) error is almost zero for pure compound, and increases as the organic mass fraction decreases, *ii*) for the surfactants (leucine, phthalic acid, succinic acid and azelaic acid), error tends to be large when (almost) pure compound is activated, reaches a minimum at the 90-50% range, and then increases again at lower organic factions. In both cases, the error at small organic fractions is consistent with the uncertainty analysis (Table 6), as molar volume uncertainty is inversely proportional to organic fraction. For the aerosol with large mass fraction of surfactant, the simple form of Köhler theory used when applying KTA (equations 1-4) do not reflect the effect of surfactant partitioning on critical supersaturation (Sorjamaa et al., 2004; Sorjamaa and Laaksonen, 2006); this, together with partial solubility effects, may introduce a bias in inferred molar volume which becomes maximum when the organic mass fraction is high. The error trends seen for leucine, phthalic acid, succinic acid and azelaic acid (Table 5) corroborate this.

The high CCN activity of Leucine is in disagreement with other published data showing Leucine to have minimal CCN activity: Huff Hartz, et al. (2006) "Cloud condensation nuclei activation of limited solubility organic aerosol" Atmospheric Environment, v40 and Raymond and Pandis (2002) "Cloud activation of single-component organic aerosol particles" Journal of Geophysical Research, v107. The authors should address this important difference.

Excellent point. We feel that the aerosol phase state is responsible for this difference, as it has been known that it can have a profound impact on CCN activity ....(Bilde and Svenningsson, 2004; Henning et al., 2005). In our study, the atomized polydisperse droplet were “softly” dried down to $\sim$ 10% RH (as measured using a RH probe inline), and under such conditions “curvature enhanced solubility” (Padró and Nenes, 2007) tends to favor the presence of water in the aerosol phase. Previous work used more aggressive drying methods (for example, Hartz el al. (2006) used a silica gel followed by an activated carbon dryer); leucine in their experiments was likely dried completely.

Technical Notes:

P3806 L10 - should read “ and provides ” with a ‘s’.

Correction has been made in the manuscript.

P3807 L15 - would be better to read “ but this is not the subject of the current study.”

Wording has been changed in the manuscript.

P3814 L12 - should be Kr-85 instead of Kr-35.

Correction has been made in the manuscript.

P3820 L12 - “powerful” seems an overstatement - replace with “useful”?

We have replaced it with “potentially powerful” for the reasons stated in the first comment.

P3820 L14 - should read “ and provides ” with a ‘s’.

Correction has been made in the manuscript.

P3829 Table 6 - please add lines to separate compounds in table.

In the conversion to ACPD format, our initial formatting changed. In the final proofing of manuscript we will have this in mind.

P3831 Fig. 2 - KR85 does not show up well

Correction made to Figure 2.

P3832 Fig. 3 - the multiply-charged particle peak seems significantly larger than other experimental activation curves published in the literature - is there something special about the authors equipment that leads to such high levels of multiply-charged particles?

The atomizer used generated a broad distribution with a large fraction of “big” particles; as a result, a large multiply-charged peak appeared in the activation curves.

References:

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Henning, S., Rosenorn, T., D’Anna, B., Gola, A. A., Svenningsson, B. and Bilde, M.: Cloud droplet activation and surface tension of mixtures of slightly soluble organics and inorganic salt, Atmos. Chem. Phys., 5, 575-582,2005.

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Interactive Discussion

Discussion Paper

Sorjamaa, R., Svenningsson, B., Raatikainen, T., Henning, S., Bilde, M. and Laaksonen, A.: The role of surfactants in Kohler theory reconsidered, Atmos. Chem. Phys., 4, 2107-2117,2004.

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