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Atmospheric
Chemistry
and Physics
Discussions

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

Anonymous Referee #1

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The authors present an interesting experimental work on water activity and surface tension of organic compounds of atmospheric interest. They use the experimental data to model the Köhler equation and cloud droplet formation. The experimental work is done with great care and the manuscript is well written. The paper contributes to our understanding of the indirect climate forcing of aerosols, a subject of high priority and well within the scope of "Atmospheric Chemistry and Physics". I find the concept of using osmometry especially interesting. I thus recommend publishing after the authors' response to a few major issues and some smaller comments.

Major issues:

1) the use of solubility: Oxalic, adipic, succinic, and pinonic acid have low solubility, as

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the authors mention in section 3.1 and as can be seen in tables 1 and 2 and in figures 1 and 2. It is, however, not clear how this low solubility is used in the Köhler modelling. It is my impression that data on critical supersaturation is presented for particles that are large enough for the droplet solution to be sub-saturated at the maximum in the traditional Köhler curve. Is this the case? In my opinion, some of the data points present in figure 4 for adipic and succinic acid should have been influenced by the solubility. Have you taken into account that there can be an even higher barrier at smaller droplet sizes caused by the solubility? I also think that your experiments could be used to determine the solubility. Have you tried to deduce the solubility from your data and how does that fit with literature values?

2) the use of surface tension data: It has lately been acknowledged that surface active compounds are depleted from the bulk as they are accumulate at the surface of small droplets [1, 2]. This cases the bulk concentration, and thus also the surface concentration and the surface tension reduction, to be smaller than expected from taking the total amount of surfactants divided by the amount of water. The substances studied in this work are all except one (pinonic acid) only weakly surface active, as concluded by the authors. The effect of surface tension reduction by these compounds is small, and taking surface to bulk distribution into account would probably not make a major difference in this case. In the case of pinonic acid, the fact that it has a low solubility makes the effect of surfactant depletion in the bulk less visible, see [2]for comparison. Even though the surface-to-bulk distribution may not make a large difference in your values, I would strongly recommend that you acknowledge the issue and argue why it is of minor importance in your results.

3) comparison with experimentally determined critical supersaturations: The authors compare their results with experimentally determined critical supersaturations for malonic and glutaric acid and with some data for pinonic acid. According to my knowledge there are more data on pinonic acid [3], adipic[4-7], and succinic acid[4, 5, 8]. There might also be data for the other acids. I also recommend that you compare with the

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results of the modelling made by Sorjamaaa et al. [2].

Smaller comments:

The title could indicate that the work is purely modelling. You could consider changing it in a way that it also demonstrates that you present important experimental work.

p. 5344, line 8: Why do you not use the same format of the Köhler curve as in eq. 1, just expressing the water activity? Eq. 2 contains some simplifications. It is for example only valid when the droplet diameter is much larger than the dry diameter i.e. the water volume can be estimated as the total droplet volume. Is this valid for all the data for which you calculated van't Hoff factors as presented in figure 3?

p. 5345: The "Experimental" section is very short. I would for example like to know the size of the droplets studied in the osmometry and surface tension measurements.

Section 3.1 and 3.2: Have you considered giving parameterisations for water activity and surface tension as a function of concentration?

p. 5347 l. 7: You state that "these compounds affect supersaturation only in the beginningĚ". I would recommend using the word "equilibrium saturation ratio" instead of "supersaturation", since the initial part of the growth often takes place already at subsaturation of water vapour.

p. 5347: In the first paragraph of section 3.2 the authors compares osmometry with other ways of measure water activity as a function of concentration. I would recommend that this section is moved, either to the introduction or to the experimental section. You should also give a reference for the electrodynamic balance.

p. 5348 l. 4: The influence of the density is mentioned. Please give values and references for the densities used.

p. 5349 l. 8- and figure 3: I like that you express your results in terms of van't Hoff factors. It would also be interesting to see how your values compare to those expected

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from dissociation constants.

p. 5350 l. 15-17: I have some problems with the expression “Evaluation of their CCN ability based on mere surface tension dataĚ”. Isn’t the CCN ability always a combination of the Kelvin effect and the water activity as in your equation 1?

The figures: The figures are in general appropriate and well made. In some of them it is difficult to follow some of the data due to overlap of data points. This is for example the case in figure 2 (difficult to see the minimum radius ratio for which there are data for the low solubility compounds) and to some degree also in figures 4 and 5. You are also using both radius (in figure 1 and 2 and eq. 1 and 2) and diameter (figures 3-7). Please stick to one of them.

Figure 1: Citric acid appears twice in the legend

Table 2, The data from the literature to compare with oxalic acid cover a wide range. Could you specify which of the values that comes from which measurement technique? I would also like to see a discussion on how well suited these methods are for measurements at such high water activities.

1. Li, Z., A.L. Williams, and M.J. Rood, Influence of soluble surfactant properties on the activation of aerosol particles containing inorganic solute. J. Atmos. Sci, 1998. 55: p. 1859-1866.

2. Sorjamaa, R., et al., The role of surfactants in Köhler theory reconsidered. Atm. Chem. Phys., 2004. 4(8): p. 2107-2117.

3. Hartz, K.E.H., et al., Cloud condensation nuclei activation of limited solubility organic aerosol. Atmospheric Environment, 2006. 40(4): p. 605-617.

4. Bilde, M. and B. Svenningsson, CCN activation of slightly soluble organics: importance of small amounts of inorganic salt and particle phase. Tellus B, 2004. 56: p. 128-134.

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5. Corrigan, C.E. and T. Novakov, Cloud condensation nucleus activity of organic compounds: a laboratory study. Atm. Environ., 1999. 33(17): p. 2661-2668.

6. Cruz, C.N. and S.N. Pandis, A study of the ability of pure secondary organic aerosol to act as cloud condensation nuclei. Atm. Environ., 1997. 31(15): p. 2205-2214.

7. Raymond, T.R. and S.N. Pandis, Cloud activation of single-compound organic aerosol particles. J. Geophysic. Res., 2002. 107: p. 10.1029/2002JD002159.

8. Prenni, A.J., et al., The effects of low molecular weight dicarboxylic acids on cloud formation. J. Phys. Chem. A, 2001. 105: p. 11240-11248.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 5341, 2007.