**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "The Cloud Condensation Nuclei (CCN) properties of 2-methyltetrols and C3–C6 polyols from osmolality and surface tension measurements" *by* S. Ekström et al.

S. Ekström et al.

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General comment: First, we would like to emphasize that the method presented in this work was developed by G. Kiss et al. (Kiss and Hansson 2004; Varga et al. 2007) who should get all the credit for it. The present work is merely applying this method. These previous works (Kiss Hansson 2004; Varga et al. 2007) also provided a detailed physical justification for this method and a comparison of its performances with on-line techniques and theoretical values. As many questions have been asked by the reviewers on these points we strongly refer to these works for details (some information has, however, been added to the manuscript).

Reviewer 1

Q1. A Table 4 has now been added to compare the method in this work with on-line techniques and theoretical values for organic acids and ddry = 100 nm. These data justify our statement of the validity of this method.

Q2. Organizing such experiments would take more than a few days as the necessary and expertise is not available in our region. But the main reason for not doing such experiments is that the compounds studied do not display good CCN efficiencies and are unlikely to display better ones with on-line techniques. We would certainly do these experiments if they were more interesting, but they seem hardly worth the effort.

Q3. Yes, as there is a direct correspondence between C and the Van't Hoff factors (see reply to Q1 of Reviewer 2 below) this method could also be used to determine Van't Hoff factors. However, the main idea of this method is to avoid using Van't Hoff factors altogether, for the reasons now added in the Experimental section (and in Q1/Rev. 2 below).

Q4. The fact that highly soluble compounds, and in particular the methyltetrols, might be efficient CCN material is a general assumption in the atmospheric community. We have tried to express this better in the introduction (we also reply to this in more detail in Q3.1/Rev. 2 below).

Q5. Same question as Q4 above and Q3.1 for reviewer 2 (references were actually given in the conclusion, p. 17246, li. 3).

Q6. This has been re-written.

Q7. A dry diameter of 60 nm seemed typical for a CCN size. 100 nm seems on the large side.

Q8. The data are now presented in the new Table 4.

Q9. Corrected.

Q10. To avoid confusion, the sentence now says "Kohler curves have been determined

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FROM experimental measurements of the osmolality and surface tension";

Q11. This information has been added to the table (now Table 3) and in the figure legends.

Reviewer 2

Q1. Van't Hoff factor vs. Osmolality The expression for water activity as function of Van't Hoff factors is:

aw =(1/Mw)/((1/Mw)+ (Sigma[(nu)i ni])/nw Mw)

Where Mw is the molar weight of water, nw the number of moles of water, ni the number of mole of each solute, and (nu)i the Van't Hoff factors, representing the effective degree of dissociation of each solute. The expression of aw as function of osmolality is:

aw =(1/Mw)/((1/Mw)+ C).

Thus, in the second expression C replaces Sigma [(nu)i ni]/(nw Mw). But there are two important differences between these expressions: first, the values of the Van't Hoff factors contain some assumptions while C is measured and thus does not involve any assumption. For substances with known Van't Hoff factors these approaches might not be very different, but for unknown mixtures (ex: aerosol extracts) accurately guessing the Van't Hoff factors is more difficult while measuring C is always possible, and with the same precision as for standard substances. The second difference, even more importantly, is that the expression with the Van't Hoff factors is only a sum of contributions the solutes, but does not take into account intermolecular or electrostatic interactions between them. C, however, takes into account all these effects, which makes significant differences on the determination of Raoult terms. This was demonstrated by Kiss and Hansson, (2004 - Table 4 text) showing that, for sulfuric acid, Van't Hoff factors underestimate the critical supersaturation, Sc, by 18-19 Thus, using osmolality and Van't Hoff factors are fundamentally different methods.

Q2. Parametrization of surface tension and osmolality as function of concentration The values for the parametrizations in Table 2 (now Table 4) at infinite dilution (c=0) are actually those for pure water, within experimental uncertainties: - for c = 0, all surface tension expressions are within ś 3 - for osmolality the value at infinite dilution should be 0. The values for the parametrizations at c=0 are between 15 and 20 We are not aware of simple analytical expressions for the surface tension or osmolality having a physical justification. The Szyskowski-Langmuir parametrization itself is empirical (S. S. Dukhin, G. Kretzschmar, R. Miller, Dynamics of Adsorption at Liquid Interfaces: Theory, Experiment, Application, Elsevier, 1995, P. 48). Moreover, the Szyskowski-Langmuir equation does not apply well to high concentrations and, in particular, does not predict the plateau displayed by experimental surface tension curves at large concentrations (this was, however, not a problem in the present work). Physical equations for osmolality do exist, but they are complex sums of electrostatic terms, unpractical for comparisons such as those of this work. But we agree that, short of proposing a physically-based parametrization, the equations presented in Table 3 (former Table 2) should be as simple as possible. We have thus simplified all these expressions into first-order ones.

Q3. Implicit factors in Köhler equation (solubility, bulk/surface partitioning...)

3.1- Whether solubility plays a role in CCN efficiency is not our idea, but a common question (or assumption) in the atmospheric community, as shown in numerous works: beside the articles referring to the potential high CCN efficiency of the methyltetrols (Silva Santos et al., 2006; Meskhidze and Nenes, 2006, quoted in our manuscript), entire projects are characterizing the organic fraction of aerosols according to its solubility for the purpose of describing its CCN properties. One example among many is Mircea et al., (2005), where the abstract states "In this study ... we show how the ... organic compounds and associated properties (e.g. solubility, surface tension...) affect the hygroscopic growth and activation of the aerosol". In any case, our manuscript does not start with the assumption that solubility plays a role in CCN efficiency, but

asks the question. As solubility does not appear explicitly in the Kohler equation, our approach was to look for potential correlations between solubility and critical supersaturation (and, more specifically, the Raoult term, as solubility is expected to play a role on the latter rather than on surface tension). This is exactly the discussion in section 3.1., p. 17243, li. 7 and following. As no correlation is observed, the conclusion is straightforward (li. 10/11).

3.2- We do not understand how we should "take into account"; the non-soluble parts of the curves. These parts were not presented on the Figures because we do not have experimental access to them. But even if we had, both the maxima of the soluble and non-soluble part of the curve are lowered in the presence of salt and the discussion can thus be based on either of these parts.

3.3- the role of bulk vs surface partitioning was not expected to be significant in this work, and thus not discussed, as none of the compounds studied displayed significant surface tension effects. Moreover, a new Table 4 now shows the agreement between our method and on-line techniques for malonic and succinic acid, indicating that bulk/surface partitioning does not contribute much to these results, even for these surface-active compounds.

Q4. See reply to the first part of the previous question (3.1).

Q5. All "radius" are now replaced by "diameter".

Q6. These concentration ranges are now added to Table 3.

Q7. Densities and molecular structures now added in a new Table 2.

Q8. The mass fractions of salts was kept constant throughout all these experiments (20 This was mentioned in the Experimental section but is now repeated in the legends.

Q9. A new Table 4 now shows the detail of Sc values obtained with our method, on-line techniques, and theoretically for malonic, succinic, and adipic acid. It is correct that the results for adipic acid with on-line techniques were scattered. The agreement for this

compound was between our method and the theoretical value. The good agreements between our method and on-line techniques were for malonic and succinic acid. This statement has now been corrected.

Q10. Same question as Q4 and first part of Q3 above: see reply 3.1.

Q11. We meant "small Raoult effect" there 8211; this has been replaced.

Q12. We explain in the Experimental section (p.17241, li. 21/22) that all the Kohler curves presented, and thus all Sc values discussed, are for a dry diameter of 60 nm. This information has now been repeated throughout the text. The

Q13.

13.1. Same question as Q3.2 above. The fact that a reduction of Sc was observed in the presence of salt implies that the compound has a limited solubility, (Bilde and Svenningsson, 2004). How would "taking into account" the non-soluble part of the curve change this conclusion ?

13.2. Same question as Q9 above. The validity of the method for surface active compounds, malonic and succinic acid, is now supported by the Sc values in Table 4.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 17237, 2008.

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