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Atmospheric
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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.

Anonymous Referee #2

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Referee comments on MS-NR: acpd-2008-0477 S. Ekström, B. Nozière, and H.-C. Hansson. The Cloud Condensation Nuclei (CCN) properties of 2-methyltetrols and C3 - C6 polyols from osmolality and surface tension measurements

The authors present critical supersaturations and Köhler curves for a series of compounds of high atmospheric interest. The methods applied are well suited for the purpose and seems to have the high accuracy needed. I find the paper well within the subject of ACP and well worth publishing after the authors response to the comments.

Main comments

page 17241 lines 15- 17 The authors state "Note that this method employs the original Köhler Eq. (1), and therefore avoids altogether the uncertainties contained in the simplified equation and in the Van't Hoff factors." I strongly disagree with this statement! Comparing equation 2 in this paper with Raoults law and using van't Hoff factor i, aw = 1/(1 + i ms Mw) , indicates to me that the osmolality is the concentration times the van't Hoff factor (with an i that can vary with concentration). Whether the experimental data are parameterized as osmolality or as a varying van't Hoff factor should not make any difference. The important, in my opinion, is that the water activity is based on accurate measurements that also cover the concentration range of interest for cloud droplet activation. I find that your method does that!

One would also like to see parameterizations that have a physical meaning and for example approaches the values for pure water when the concentration approaches zero. Looking at the parameterizations given in table 2, we can see that their values for infinite dilution (c=0) are different and are not those of pure water. Would it be possible to let the constant in the surface tension parameterization be the surface tension of pure water and the constant in the osmolality parameterization be zero? Why do you not use the Szyszkowski-Langmuir parameterization of the surface tension: surface tension= surface tension for water - A T ln(1+B c).

The statement in lines 15-17, page 17241, is especially unfortunate since there are, at least, two effects that are touched on in this paper, but that are not explicitly included in equation 2, and not fully discussed in the text. 1) Solubility is brought forward as an important parameter for cloud droplet activation, but I can only find one place in the paper were the authors make use of the solubility data: the effect is indicated with dashed lines for the adipic and succinic acids in figure 3. However, when the effect of mixing with salts is discussed, this part of the Köhler curve is not taken into account, and the critical supersaturation of the organic acids is taken as the maximum of the traditional Köhler curve (solid line) even though the dashed line reaches to higher values. 2) The effect of bulk to surface partitioning of surfactants is not taken into account. The

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values of c, to be used in the parameterizations in table 2, cannot be calculated as the total amount of the organic compound per unit of water. The amount in the bulk should be used (total minus the amount at the surface). For the compounds studied here, the difference might not be so pronounce, but for highly surface active compounds the methodology can give much too low values for the critical supersaturation (Sorjamaa et al. 2004)

Detail comments:

p17238 l 10. The authors state that "Contrary to what expected , none of these compounds displayed a critical supersaturation lower than those of inorganic salts or organis acids." I just wonder why one would expect lower critical supersaturations for the substances studied in this paper. Are there any theoretical considerations behind this expectation?

P. 17240 l. 18 and 20. Radius is used here, but the figures show diameters. Please be consistent and clear about this.

P 17240 l. 18 The authors say that the concentration is varied between 0 and 2 M. It would be good to give the lowest analyzed concentration instead of just 0. This could be given in table 2, as an indication of the range over which the parameterizations are valid.

P 17240 l 22-25 and table 1. Densities are discussed briefly here. I would have liked all densities used in the calculation to be given in table 1, together with molar weights, chemical formulas and some indication of the molecular structure. This information would really make the paper much more useful!

P. 17241 l. 26-27 and table 2 as well as figures 4 and 5: I would like to see the information on mass fractions of salt in the mixed particles to be more visible. Why not mention it in the legends of figures 4 and 5 and in table 2?

P. 17242 l. It is surprising that you find excellent agreement for adipic acid between your method and the measurements using CCN spectrometers. Would be interesting to see how you made the comparison and the values that you consider as being in excellent agreement. I thought that there were some reproducibility problems in the CCN spectrometer data for adipic acid, due to their being very sensitive to trace amounts of impurities?

P. 17243 l. 10-12 This is the same issue as brought up in the abstract: with the expectations of the solubility controlling the CCN efficiency. What are they based on?

P. 17244 l. 7 Does "low water activities" refer to values close to 1 or close to 0?

P. 17244 l. 21 The values given here, for which particle size are they valid and for which fractions of inorganic salt? Do they also take into account the affect of solubility (the dashed part of the curves in figure 3?

P. 17245 l. 2-5 I cannot see how the authors can draw this conclusion, since the critical supersaturation that they refer to for the pure mannitol particles does not take into account the effect of solubility. The same argument goes for some of the following conclusions (lines 8-9 and to some degree also lines 13 -15 on the same page).

Based on the comments above, I also disagree with the statement that the method is valid "even when applied to compounds having significant surface tension effects". I cannot see that there are any data in this paper supporting this conclusion. If there are, please discuss them in more detail and make a quantitative comparison with direct analysis of critical supersaturations.

Thanks for some very interesting reading and congratulations to a very useful method!

Sorjamaa, R., Svenningsson, B., Raatikainen, T., Henning, S.,Bilde, M., and Laaksonen, A.: The role of surfactants in Köhler theory reconsidered, Atm. Chem. Phys., 4, 2004.

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