

Interactive comment on “The potential contribution of organic salts to new particle growth” by K. C. Barsanti et al.

Anonymous Referee #1

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The manuscript studies the potential contribution of organic salts formed from low - molecular weight (MW) species to new-particle growth in the atmosphere, using classical thermodynamic modeling methods. The topic and results of the manuscript are highly relevant, and are likely to be of interest to a large fraction of the readers of ACP. The manuscript is well written, and for the most part understandable also by readers without extensive knowledge of the modeling methods used.

The authors present two central conclusions in this study. First, they find that given a sufficiently high concentration of low-MW amines compared to that of ammonia, amines may significantly contribute to the formation of organic salts in atmospheric aerosol particles, and thus assist their growth (and possibly also play some small role in their formation?). This is at least qualitatively similar to what Kurtén et al. (some re-

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sults in ACP, 8, 4095, 2008) have found for small amine- or ammonia-containing sulfate clusters, albeit using a very different modeling approach and focusing only on the very smallest nucleating clusters. At gas-phase amine:ammonia concentration ratios close to one, the precise chemical identity of the amine (specifically, its Henry's law constant, and even more importantly, the pKa value of the protonated cation) was shown by the authors to play a large role in determining the amine:ammonia ratio of the particulate phase.

Second, the authors have carried out a sensitivity analysis to determine the effect of parameter choices on the predicted extent of organic salt formation for a set of atmospherically relevant test systems. This is extremely important as some of the parameters needed for the modeling seem to be associated with huge error bars and uncertainties. They find that while parameters such as Henry's law constants, pure-liquid vapor pressures and surface tensions play some role, the most important parameters controlling the extent of salt formation are the difference in the pKa values of the salt-forming acid-base pair and the activity coefficients of the ions. This seems reasonable from a chemical point of view, as these parameters are the ones that describe most of the chemical interactions between the acid and base molecules, rather than just the properties of the pure compounds. For the system studied (dimethylamine + acetic or pinic acid in aqueous solution, with initial mole fractions of 0.25 for both acid and base) most of the organics were predicted to be in salt form regardless of the parameter choice, which again seems chemically reasonable given the large pKa difference.

I am not able to comment on the validity of the precise details of all the modeling methods used here, but based on the references given in the manuscript they seem to be, for the most part, previously tested and benchmarked for relevant or comparable systems. Some of the methods seem to be applied quite far outside their original field of validity (e.g. in the case of ion activity coefficients significantly larger than one), but this is probably unavoidable given the complicated nature of the systems studied.

Some comments and suggestions:

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1)At the top of page 20725, the supersaturations given are presumably those of water. This may not be immediately apparent to readers unfamiliar with CCN research, so this should perhaps be explicitly stated.

2)While the discussion in section 3.1 is relatively easy to read, section 3.2 is quite hard to follow for a non-expert. I understand that the authors would like to keep the text compact and use shorthand notation, but perhaps some more explanations would be appropriate here? The Figures (2 and 3) corresponding to this section are also slightly unclear. For example, according to the caption there should there be a "DMAg" bar in Fig 2, but it is nowhere to be seen. This is presumably because the value is very close to zero. Might a logarithmic scale therefore be more appropriate here? Alternatively, the order of magnitude or range of the DMAg values might be mentioned in the text, and the figure caption could state that DMAg is too small to be shown.

3)A large part of the discussion in Section 3.2 (and thus, a large fraction of the conclusions of the whole paper) is centered on the role of the value chosen for the parameter C in the Davies equation (as reported by Samson et al., 1999). Yet, no explanation or discussion as to the physical or chemical significance or interpretation of this parameter is given. I understand that the modeling employed here is based on a combination of many, many different techniques, and that explaining all of them to a non-expert reader would require far too much space. Also, based on the Samson et al. (1999) paper, the parameter C does not seem to have any obvious physical interpretation; it is just an empirical term added to the (perhaps somewhat more generally known) extended Debye-Hückel model that is proportional to the ionic strength rather than its square root. Nevertheless, given that this "C" parameter seems to be of so crucial importance, a few lines of background explanations should be devoted to it. Perhaps even the modified Davies equation itself could be given in the manuscript, since it seems to be rather central to the discussion.

4)It is a bit unclear to me how the activity model of Samson et al. (1999) corresponds or compares to those studied in Tong et al (2008), other than the fact that it is uncoupled.

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The authors use the study by Tong et al. (2008) to justify using the Davies equation, but it is not one of the four models being compared therein. Was the Davies equation used because the CSB and ADDEM decoupled models studied in Tong et al (2008) need some data that is unavailable for the systems studied here? Or is it expected to perform better for these systems? This issue should be briefly addressed.

5)The reference states for the activity coefficients (especially those of the ions) should be given.

6)The Samson et al. (1999) paper in which the modified version of the Davies equation is defined only contains data on ion activity coefficients below unity. How reliable, even qualitatively, are predictions of ion activity coefficients $\gg 1$ using this equation? The manuscript already contains some discussion on the subject but this issue is still a bit unclear.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 20723, 2008.

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