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Atmospheric
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Discussions

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

K. C. Barsanti et al.

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The authors would like to thank the reviewers for their thoughtful reviews, and constructive comments and suggestions.

Reviewer #1

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.

Agreed, top of p. 20725 now reads: Recent modeling work by Spracklen et al. (2008) indicates that NPF in the boundary layer may significantly affect global CCN concentrations, with predicted increases in the global mean of 3-20% at 0.2% water supersaturation and of 5-50% at 1% water supersaturation.

1. *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?*

Section 3.2 has been rewritten in an effort to improve the clarity.

Fig. 2 illustrates the predicted equilibrium mass fractions of DMA in the gas phase (DMA$_g$) and particle phase (DMA$_p$+ DMAH$^+$); and the sensitivity of organic salt predictions to $p^\circ_L$and Δp$K_a$values(organic salt formation w/AcOH, ST 2$_{AcOH}$, vs. w/pinic acid, ST 2$_{pinic}$), to σ_m estimation (ST 2$_{AcOH,\sigma}$), and to ζestimation (ST 2$_{AcOH,\zeta}$). Most of the DMA mass is predicted to be in the particle phase as DMAH$^+$, with DMAH$^+_{pinic}$ $>$ DMAH$^+_{AcOH}$ $>$DMAH$^+_{AcOH,\sigma}$ $>$ DMAH$^+_{AcOH,\zeta}$ (see DMA$_g$, Fig. 2). The same is true for the acids, AcOH (ionic form)in ST 2$_{AcOH}$ and pinic acid (ionic form)in ST 2$_{pinic}$(see HA$_g$, Fig. 2). Regarding sensitivity to $p^\circ_L$and Δp$K_a$values, ST 2$_{pinic}$ (σ_m =26.84dyn cm^{-1}) is predicted to have a greater mass fraction of DMAH$^+$ than ST 2$_{AcOH}$(σ_m =25.74dyn cm^{-1}). While the estimated surface tension is slightly greater in the system with pinic acid and $\zeta_{pinic} > \zeta_{acetic}$, it is the much lower $p^\circ_L$of pinic acid than that of acetic acid, and the greater Δp$K_a$for the organic salt of pinic acid (p$K_{a,DMA}$ - p$K_{a,pinic}$ = 6.00) than that of acetic acid, that contribute to the greater extent of organic salt formation.

Regarding sensitivity to surface tension, for ST 2$_{AcOH}$(initial composition: X_{water} = 0.5, $X_{acid} = X_{base}$= 0.25),σ_m is calculated as described in Sect. 2.2. That calculated value is similar to $\sigma_m$for a *non-aqueous* organic mixture when calculated using a simple binary approach, $\sigma_m = X_{acid}\sigma_{acid} + X_{base}\sigma_{base}$. Experimental data have shown that measured $\sigma_m$values for ionic liquids are typically greater than that for non-ionic organic liquids but less than that for pure water (Greaves et al., 2006). For dilute *aqueous* organic salt solutions, the presence of amines and NH_3 tends to lower surface tension (Mmereki et al., 2000; Donaldson, 1990), while the presence of an inorganic acid and subsequent salt formation increases surface tension (Weissenborn, 1996). Raatikainen et al. (2008) found that for organic salt solutions with amines and inorganic acids, $\sigma_{acid} > \sigma_m >> \sigma_{base}$. Therefore, in ST $2_{AcOH,\sigma}$ $\sigma_m$was set $=\sigma_w$as an approximate upper limit for the surface tension of the organic salt solutions considered here. While the increased surface tension of the mixture does result in a predicted increase in DMA_g and thus a decrease in predicted particle-phase DMA and AcOH, this effect is small compared to the predicted effects of activity ($a_i = X_i\zeta_i$), discussed below.

Regarding sensitivity to activity coefficients, the standard and modified Davies equations are typically valid for solutions with ionic strengths $<$ 0.5 M. Samson et al. (1999) found that for more concentrated ionic solutions (0.5 to 1.5 M) better agreement with experimental data was achieved by reducing the parameter Cin Eq. (5) from 0.2 to 0.15. While the ionic strengths of the solutions considered here are significantly greater than 1.5 M, models that are valid at higher ionic strengths require parameters fit to experimental data, which are unavailable for systems of the type considered here. For ST $2_{AcOH,\zeta_{ions}}$were calculated using the modified Davies equation with C = 0.15. The standard Davies equation with b = 0.2 and b = 0.3 also was used to calculate ζ_{ions}. The range of estimated $\zeta_{ions}$is significant, from $\sim 10^0$ to 10^2, and therefore has the greatest affect on the predicted extent of organic salt formation. However, even when $\zeta_{ions} \sim 10^2$ (b = 0.3), the mass fraction of $DMAH^+ \approx 0.9$ (ST $2_{AcOH,\zeta}$). As the estimated ζ_{ions}values increase, equilibrium shifts from $DMAH^+$ towards DMA_p and DMA_g, and subsequently decreases the predicted extent of organic salt formation.

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.

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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

Fig. 2 and 3 have been combined, showing DMA$_g$ and DMA$_p$ on the same figure, on a logarithmic scale.

1. *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.*

In Sections 2.2 and 3.2, additional background information has been included on the standard and modified Davies equations and the related empirical parameters (e.g., C). The modified Davies equation itself is now shown in Section 2.2.

Section 2.2: As a first approximation, values of $\zeta_i$for neutral species were calculated using UNIFAC (Fredenslund et al., 1977); values of $\zeta_i$for ions were calculated using the Davies equation. The Davies equation is composed of two terms. The first term is based on the Debye-Hückel equation and accounts for long range ion-ion interactions in dilute aqueous ionic solutions ($<\ \sim$0.01 mol L^{-1}or M); the second term is an empirical term and accounts for short range ion-ion interactions and solvation effects in more concentrated aqueous ionic solutions ($<\ \sim$0.5 M). A modified form of the Davies equation is given by Samson et al. (1999):

Modified Davies equation here

where γ_i is the molal scale activity coefficient ($\zeta_i = \gamma_i$ (m_iMW$_w$)/(X_i*1000), m_i is the molality of i). The parameters$A$ and B are dependent on the dielectric constant, density, and temperature of the solvent, in the case of the Davies equation, water at 298 K and 1 atm (=1.1744 kg$^{1/2}$mol$^{-1/2}$and 3.285 x 10^9 kg$^{1/2}$mol$^{-1/2}$m^{-1}, respectively); I is the ionic strength (= $\Sigma_i\ \ m_i z_i^2$, z is the charge on ion i), and a_i is the effective diameter of i(= 3 x 10^{-10} m). In the standard Davies equation, the empirical term takes the form *bI*, where b = 0.2 to 0.3; in this modified Davies equation C = 0.2 (Samson et al., 1999). The reference state for the ionic species is infinite dilution, defined for the mean ionic activity coefficient such that as $m_+m_-\ \ \rightarrow$ 0, $\gamma_+\gamma_-\ \ \rightarrow$ 1. The reference state for the neutral species, including water, is the pure liquid; as $X_i\ \ \rightarrow$ 1, $\zeta_i\ \ \rightarrow$ 1.

Section 3.2: See third paragraph under response to comment 2.

1. *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.*

Correct, the reference to Tong et al. (2008) was only in regard to the fact that the approach used here was uncoupled. The reference does not seem necessary and has been removed.

Reviewer #2

$1.)$ *It is unclear to this reviewer why both 100:1 and 1000:10 NH3:DMA gas-phase*

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ratios are cited in Table 2 given that the results are, as expected, are identical.

Agreed, the columns have been condensed.

2.) *In Figure 2 the concentration ratios of NH3:Amine range from 1:1 to 1:100. Given that the atmospherically relevant concentrations are probably less than 1:1, it would be very informative if the authors could add additional data points at NH3:Amine ratios of 10:1 and 100:1. While it is mentioned on line 14 of page 20732 that, "The same would be true when NH3 greatly exceeds DMA in the gas phase. In such cases, ci becomes the dominant driving force for organic salt formation." it would be good to see this effect quantitatively on the graph.*

Data points at NH_3:Amine ratios of 100:1 and 10:1 have been added to Fig. 2.

3.) *The fraction of dimethylamine in the gas phase is said (both in the text and in the figure caption) to be shown in Figure 2, but there is no indication of gas-phase species in Figure 2. The reader is left to assume that the fraction in the gas phase is negligibly small. If this is the case, it should be clearly noted on the figure and in the text.*

Agreed, see response to Reviewer 1, comment 2.

4.) Given the importance of ζ estimates to the results presented and given that terminology changes from one text to another, it would seem reasonable to explicitly write the Davies equation in the text and to give a brief explanation of how and why the values of C for this work were chosen. I realize this is not the focus of the work, but it is a bit frustrating to see multiple references to the parameter C without having the functional form of its relationship to activity written out in the text.

Agreed, see response to Reviewer 1, comment 3.

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

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The following sentence regarding reference states for the activity coefficients has been added in Section 2.2: The reference state for the ionic species is infinite dilution, defined for the mean ionic activity coefficient such that as $m_+m_- \rightarrow 0$, $\gamma_+\gamma_- \rightarrow 1$. The reference state for the neutral species, including water, is the pure liquid; as $X_i \rightarrow 1$, $\zeta_i \rightarrow 1$.

1. *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 $>>$ 1 using this equation? The manuscript already contains some discussion on the subject but this issue is still a bit unclear.*

Due to the high ionic strengths of the solutions considered, the actual values of the ionic activity coefficients estimated using the modified Davies equation can not be considered reliable (it is not even clear that these values are actually $> \quad >$1). However, the values of the ionic activity coefficients can be used to probe the sensitivity of organic salt formation to activity coefficient estimation. Section 3.2 has been rewritten in an attempt to make this clearer (e.g., actual values of activity coefficients have been removed; organic salt predictions using the Davies and modified Davies equations are compared, better illustrating sensitivity to activity coefficient estimation). See third paragraph under response to Reviewer 1, comment 2. The concluding sentences in the paper further assert that the estimation methods are not necessarily reliable for the systems considered, but used to illustrate the sensitivity of organic salt formation to various parameters, and that additional data are needed desperately: the results herein are intended to provide an indication of the sensitivity of organic salt formation to various parameters considered and the overall potential for organic salt formation, rather than the absolute extent of organic salt formation for atmospherically relevant systems. Experimental data will greatly improve our understanding of organic salt formation in atmospherically relevant systems, and our ability to accurately predict the

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extent to which such salts contribute to the mass growth of existing aerosols and newly formed particles.

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