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**Contribution of  
organic salts to new  
particle growth**

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# The potential contribution of organic salts to new particle growth

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## Abstract

Field and lab measurements suggest that low-molecular weight (MW) organic acids and bases exist in accumulation and nucleation mode particles, despite their relatively high pure-liquid vapor pressures. The mechanism(s) by which such compounds contribute to the mass growth of existing aerosol particles and newly formed particles has not been thoroughly explored. One mechanism by which low-MW compounds may contribute to new particle growth is through the formation of organic salts. In this paper we use thermodynamic modeling to explore the potential for organic salt formation by atmospherically relevant organic acids and bases for two system types: one in which the relative contribution of ammonia vs. amines in forming organic salts was evaluated, the other in which the decrease in volatility of organic acids and bases due to organic salt formation was assessed. The modeling approach employed relied heavily on group contribution and other estimation methods for necessary physical and chemical parameters. The results of this work suggest that amines may be an important contributor to organic salt formation, and that experimental data are greatly needed to improve our understanding of organic salt formation in atmospherically relevant systems and to accurately predict the potential contribution of such salts to new particle growth.

## 1 Introduction

The number of aerosol particles acting as cloud condensation nuclei (CCN) is a critical factor in understanding and accurately predicting the feedbacks between aerosols and climate (Novakov and Penner, 1993). It has been suggested that new particle formation (NPF), the formation of stable nuclei in the atmosphere and their subsequent growth to particles of a measurable size (typically >3 nm), is an important contributor to CCN (e.g. Laaksonen et al., 2005; Kerminen et al., 2005; Sotiropoulou et al., 2006). 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

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mean of 3–20% at 0.2% supersaturation and of 5–50% at 1% supersaturation. Such predictions rely on assumptions and approximations of the identities, quantities, and properties of the compounds contributing to particle growth. Those assumptions will have a direct effect on CCN predictions because of their importance in determining particle hygroscopicity, as well as growth rates and therefore particle size. To illustrate, Spracklen et al. (2008) conclude that more accurate model predictions cannot be achieved without better understanding of growth rates, which in turn will require a better understanding of the compounds contributing to such growth.

Freshly nucleated particles grow by coagulation and predominately, condensation (Weber et al., 1995). Correlations between sulfuric acid ( $\text{H}_2\text{SO}_4$ ) concentrations and particle growth rates indicate that  $\text{H}_2\text{SO}_4$  condensation can explain some, and occasionally all, observed particle growth (Stolzenburg et al., 2005). Growth rates in excess of  $\text{H}_2\text{SO}_4$  condensation suggest that other compounds may be condensing (Weber et al., 1997) or other mechanisms such as reactive uptake may be important (Zhang and Wexler, 2002). In one of the early studies investigating chemical composition of particles formed during NPF events, it was found that event particles were distinguishable from non-event particles by the significant presence of dimethylammonium, possibly present as dimethylammonium sulfate or dimethylammonium bisulfate (Mäkelä et al., 2001). More recent studies employing a Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS) support the findings of Mäkelä et al. (2001) and others (e.g. O'Dowd et al., 2002; Zhang et al., 2004) that indicate organics contribute to the growth of newly formed particles, and likely include compounds such as low-molecular weight (MW) amines and carboxylic acids (Smith et al., 2008).

In general, based solely on their pure-compound vapor pressures ( $p_i^0$ ), one would not expect low-molecular weight amines and carboxylic acids to contribute to condensational growth of newly formed particles. For example, the  $p_i^0$  value of dimethylamine (C2) at 293 K is  $\sim 2 \times 10^0$  atm and acetic acid (C2) is  $\sim 2 \times 10^{-2}$  atm, while calculations based on observed growth rates of 1–10  $\text{nm hr}^{-1}$  (Kulmala et al., 2004) lead to saturation vapor pressures ( $p_i$ ) of  $\sim 4 \times 10^{-16}$  atm for condensing compounds. Even con-

densation of higher-MW carboxylic acids (e.g. up to C30 diacids) would be negligible at the earliest stages of growth since the Kelvin effect of nanometer-sized nuclei prohibits such compounds from contributing to condensational growth (Zhang and Wexler, 2002). The apparent discrepancy between the  $p_L^\circ$  values of compounds thought to be contributing to growth of newly formed particles and required  $p_i$  values suggests that mechanism(s) other than simple condensation of observed organics contribute to new particle growth.

At least two possibilities exist for the contribution of low-MW organic compounds to new particle growth: (1) the formation of accretion products, and (2) the formation of organic salts. Accretion products are higher-MW/low-volatility compounds formed by reactions of organic compounds with each other and/or other atmospheric constituents (e.g. H<sub>2</sub>O, H<sub>2</sub>SO<sub>4</sub>); and can occur in the gas phase, particle phase, and/or heterogeneously (Barsanti and Pankow, 2004). Accretion reactions have been used to explain the apparent discrepancy between measured and calculated contributions of semi-volatile compounds to larger particles (e.g. Jang and Kamens, 2001; Tobias and Ziemann, 2001; Barsanti and Pankow, 2005, 2006). Additionally, Zhang and Wexler (2002) used heterogeneous accretion reactions to explain the contribution of organics to newly formed particles. While the contributions of accretion products are indeed a possibility that is being explored, here we will focus on the potential contribution of organic salts.

It is known that ammonia (NH<sub>3</sub>) neutralizes particles by reacting with H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> (nitric acid) to form inorganic salts (Jaeschke et al., 1998; Seinfeld and Pandis, 1998), which concurrently shifts the equilibrium of the participating species towards the particle phase (Pankow, 2003; Pinder et al., 2007). Analogously, it has been suggested that in the presence of excess inorganic base, organic acids act to neutralize particles (Mircea et al., 2005; Trebs et al., 2005; Metzger et al., 2006), thereby forming organic salts and shifting the equilibrium of the acids and bases towards the particle phase. Angelino et al. (2001) used laboratory experiments to show that organic salt formation could explain the significant presence of amines in ambient particles. Additionally, the presence of organic salts has been invoked to reconcile modeled and measured

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hygroscopic growth and CCN activity of aerosols (Mircea et al., 2005; Metzger and Lelieveld, 2007); which has been supported by recent experimental results of Dinar et al. (2008).

Here we present a thermodynamic consideration of the potential contribution of organic salt formation to the growth of newly formed particles. Equilibrium modeling is applied to two system types: the first addresses the relative importance of amines vs. ammonia in forming organic salts; the second evaluates the decrease in volatility of acids and bases due to the formation of organic salts. The focus of this work is primarily on organic salt formation from low-MW acids and bases, such as dimethylamine (DMA) and acetic acid (AcOH). Organic salt formation involving a higher-MW organic acid, pinic acid, also is considered. The implications of the results are discussed with regard to other atmospherically relevant acids and bases as well. The modeling approach employed relies heavily on group contribution and other estimation methods to obtain necessary physical and chemical parameters, which ultimately highlights the need for experimental studies on organic salts with atmospherically relevant compositions, as such salts may be important contributors to new particle growth.

## 2 Methodology

### 2.1 Equilibrium partitioning of atmospherically relevant organic acids, bases, and their salts

The extent to which organic acids and bases exist in nanometer-sized particles depends on their concentrations ( $c_i$ ); pure-liquid vapor pressures ( $\rho_{L,i}^\circ$ ) or Henry's Law constants ( $K_{H,i}$ ); acid dissociation constants ( $K_{a,i}$ ); and activity coefficients (mole scale,  $\zeta_i$ ). Additionally, the liquid molar-volume of each constituent ( $V_i$ ) and the surface tension of the particle mixture ( $\sigma_m$ ) will play a role when curvature corrections are considered. When thermodynamic equilibrium is assumed, the following equations can be used, along with mass and charge balance equations, to estimate the amounts of

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acids, bases, and salts in each phase (where  $X_i$  is mole fraction):

$$p_i(\text{atm}) = p_{L,i}^\circ \zeta_i X_i \quad (1)$$

$$K_{\text{a,acid}} = \frac{\zeta_{\text{H}^+} X_{\text{H}^+} \zeta_{\text{A}^-} X_{\text{A}^-}}{\zeta_{\text{HA}} X_{\text{HA}}} \quad (2)$$

$$K_{\text{b,base}} = \frac{\zeta_{\text{H}^+} X_{\text{H}^+} \zeta_{\text{B}} X_{\text{B}}}{\zeta_{\text{BH}^+} X_{\text{BH}^+}} \quad (3)$$

5 Including curvature corrections in Eq. (1), based on the Kelvin equation, leads to:

$$p_i = p_{L,i}^\circ \zeta_i X_i \exp\left(\frac{V_i 2\sigma_m}{rRT}\right) \quad (4)$$

where  $r$  is particle radius (cm),  $R$  is the ideal gas constant ( $\text{dyn cm mol}^{-1} \text{K}^{-1}$ ), and  $T$  is temperature (K). When considering partitioning to and from a dilute aqueous particle, Henry's law applies and  $p_{L,i}^\circ$  in Eqs. (1) and (4) becomes  $K_{\text{H},i}$ .

## 10 2.2 Physical and chemical property data sources and estimation methods

Limited physical and chemical property data exist for organic acids and bases in systems of the type considered here. Organic salts have been studied widely as ionic liquids: two component organic salts that are liquids at room temperature and contain little or no water. Much data exists on the physical and chemical properties of organic salts in such systems (Zhang et al., 2006; Greaves and Drummond, 2008; and references therein); though it is not entirely clear how applicable such data are for atmospherically relevant systems, which may contain varying amounts of water and multiple organic and inorganic acids and bases. For atmospheric aerosols, equilibrium partitioning is often considered for two phases: (1) a dilute aqueous phase with neutral organic compounds and ionized inorganic compounds, and (2) a mostly organic phase

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with neutral organic compounds. In this work, assumptions have been made about the composition of nanometer-sized particles, in part to make the best use of available data, estimation methods, and models.

When experimental data were not available for properties of interest, estimation methods were used. For most acids and bases considered,  $p_{L,j}^{\circ}$  values were estimated using the Antoine equation with parameters obtained from NIST Chemistry WebBook (Linstrom and Mallard, 2005; <http://webbook.nist.gov/chemistry/>);  $K_H$  values also from NIST Chemistry WebBook; and  $K_a$  values from Hall (1957; <http://www.webqc.org/pkaconstants.php>) and the CRC Handbook of Chemistry and Physics (Lide, 2008). When not available,  $p_{L,j}^{\circ}$  values were estimated using the SIMPOL group contribution method (GCM) of Pankow and Asher (2008). The  $K_a$  value for pinic acid was estimated using SPARC (Hilal et al., 1995; <http://ibmlc2.chem.uga.edu/sparc/>). As a first approximation, values of  $\zeta_i$  for neutral species were calculated using UNIFAC (Fredenslund et al., 1977); values of  $\zeta_i$  for organic ions were calculated using the Davies equation, with a modification of the parameter  $C$  used by Samson et al. (1999) for concentrated ionic solutions. This decoupled approach to treating activity has been shown to work reasonably well for aqueous solutions with neutral organics and inorganic ions when compared with currently available models employing a fully-coupled approach (Tong et al., 2008).

It was assumed here that partial molar volumes were equivalent to pure-compound molar volumes ( $V_i$ ), and were estimated using ACD/ChemSketch (2006). Values of  $\sigma_i$  also were estimated using ACD/ChemSketch (2006). Values of  $\sigma_m$  were calculated using the method of Sprow and Prausnitz (1966) as described in Poling et al. (2001); using the method of Tyn and Calus (1975) to determine molar volume at boiling temperature and the method of Suarez et al. (1989) to calculate the surface area of each component, also as described in Poling et al. (2001). The second-order GCM of Constantinou and Gani (1994) was used to estimate the critical volume ( $V_c$ ) of pinic acid. For all other compounds  $V_c$  values were obtained from the CRC Handbook of Chemistry and Physics (Lide, 2008). The values of  $\sigma_m$  were calculated based on the initial

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compositions of the particles, and thus do not take into account the presence of ions. Implications of this approximation are discussed further in Sect. 3.2. While models are available that take into account the presence of inorganic and organic ions (Li and Lu, 2001; Raatikainen et al., 2008), such models require parameters fit to experimental data, which are unavailable for systems of the type considered here. Physical and chemical property data for all compounds considered are summarized in Table 1.

### 2.3 Initial particle composition and system types

In this work we evaluated the potential for organic salt formation in the atmosphere by considering equilibrium partitioning of acids and bases between the gas and particle phases for two system types, differentiated by the assumed initial composition of nanometer-sized particles. The first system type (ST 1) was designed to investigate the relative importance of amines vs.  $\text{NH}_3$  in forming organic salts by considering partitioning of gas-phase amines,  $\text{NH}_3$ , and an organic acid to a dilute aqueous particle. Concentrations of amines were based on ambient measurements in southern Sweden (Grönberg et al., 1992). Similar levels have been reported, on the order of tens or less of ppt, for ambient measurements at other locations (e.g. Akyüz, 2007), while much higher levels also have been reported, on the order of tens to hundreds of ppb (Rabaud et al., 2003; Rampfl et al., 2008).

The second system type (ST 2) was designed to investigate the contribution of organic salt formation to the reduction in volatility of organic acids and bases from nanometer-sized particles. In this system type, gas/particle partitioning of acids and bases was considered for aqueous particles with initial organic acid and base mole fractions of  $X_{\text{acid,initial}}=0.25$  and  $X_{\text{base,initial}}=0.25$ . Since the focus of this work is on low-MW organic acids and bases, AcOH and DMA were chosen as representative atmospheric organic compounds for both system types. For ST 1, organic salt formation involving other low-MW aliphatic amines also was considered. For ST 2, organic salt formation involving a higher-MW organic acid, pinic acid, also was considered. For both system types, implications of the results for other atmospherically relevant organic

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acids/bases are discussed.

### 3 Results

#### 3.1 Salts of acetic acid, amines, and ammonia in dilute aqueous particles, neglecting activity and curvature corrections (ST 1)

5 For an aqueous nanometer-sized particle, the relative amounts of particle-phase DMA and  $\text{NH}_3$  predicted at equilibrium are shown in Table 2. Activity and curvature corrections have been neglected for this dilute system. Regarding the latter, reported surface tension measurements indicate that  $\sigma_m$  of dilute aqueous DMA solutions (Hyvärinen et al., 2004) are less than  $\sigma_m$  of dilute aqueous  $\text{NH}_3$  solutions (Paul and Chandra, 2005).  
10 The results presented in Table 2 are for assumed steady-state, gas-phase levels of 100 ppt AcOH, 1–10 ppt DMA, and 100–1000 ppt  $\text{NH}_3$ . The results suggest that when the level of gas-phase DMA ( $\text{DMA}_g$ ) is within an order of magnitude (or greater) of gas-phase  $\text{NH}_3$  ( $\text{NH}_{3,g}$ ), DMA ( $\text{DMA}_p + \text{DMAH}^+$ , where  $\text{DMA}_p \ll \text{DMAH}^+$ ) will be more abundant in the particle phase than  $\text{NH}_3$  ( $\text{NH}_{3,p} + \text{NH}_4^+$ , where  $\text{NH}_{3,p} \ll \text{NH}_4^+$ ). This  
15 is due to DMA and  $\text{NH}_3$  having Henry's Law constants of similar magnitude, 31 and  $62 \text{ M atm}^{-1}$  respectively; but DMA having significantly greater basicity than  $\text{NH}_3$ , with  $\Delta pK_a$  ( $pK_{a,\text{base}} - pK_{a,\text{acid}}$ ) = 5.88 for DMA and AcOH and  $\Delta pK_a = 4.49$  for  $\text{NH}_3$  and AcOH. It should be noted that the predicted amounts of DMA in the particle phase are greater than what would be predicted for equilibration of DMA alone (i.e. based on  $K_H$  value  
20 only, with no acid and therefore no organic salt formation). Thus when considering the potential for other atmospherically relevant amines to form organic salts, in addition to their concentrations and  $K_H$  values,  $pK_a$  (or  $\Delta pK_a$ ) values must be considered.

Table 3 lists the low and high levels measured by Grönberg et al. (1992) for five aliphatic amines, and their  $K_H$  and  $pK_a$  values. Those values, along with gas-phase amine levels reported by Rampfl et al. (2008), were used here to represent a range  
25 of possible values for ambient amines. For these general considerations, the fraction

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of amines in the particle phase ( $f_{\text{amines}} = n_{\text{amines,p}}/n_{\text{total base,p}}$ , where  $n$  is mols) is shown in Fig. 1, as a function of gas-phase  $\text{NH}_3$  and amine levels, and  $K_{\text{H}}$  and  $\Delta pK_{\text{a}}$  values ( $pK_{\text{a,amine}} - pK_{\text{a,AcOH}}$ ). From Fig. 1 it can be seen that when the level of gas-phase amines is on the order of gas-phase  $\text{NH}_3$ ,  $K_{\text{H}}$  and  $\Delta pK_{\text{a}}$  values play a significant role in determining the amount of amines vs. the amount of  $\text{NH}_3$  in the particle phase. While DMA was predicted to be more abundant than  $\text{NH}_3$  in the particle phase when the levels of  $\text{DMA}_{\text{g}}$  were within an order of magnitude of  $\text{NH}_{3,\text{g}}$ , amines with  $K_{\text{H}}=10$  and  $\Delta pK_{\text{a}}=5.00$  are predicted to be less abundant in the particle phase even with equivalent levels of amines and  $\text{NH}_3$  in the gas phase. For these particular  $K_{\text{H}}$  and  $\Delta pK_{\text{a}}$  values, at the 1:1 gas-phase ratio, increasing  $\Delta pK_{\text{a}}$  is predicted to play a greater role than increasing  $K_{\text{H}}$  in promoting organic salt formation. Also from Fig. 1 it can be seen that when amines greatly exceed  $\text{NH}_3$  in the gas phase,  $K_{\text{H}}$  and  $\Delta pK_{\text{a}}$  values become less important in predicting the relative contribution of amines vs.  $\text{NH}_3$  to organic salt formation. The same would be true when  $\text{NH}_3$  greatly exceeds DMA in the gas phase. In such cases,  $c_i$  becomes the dominant driving force for organic salt formation.

### 3.2 Volatility of organic acids and dimethylamine in aqueous particles containing organic salts, including activity and curvature corrections (ST 2)

In Fig. 2, the predicted equilibrium mass fractions of DMA in the gas phase ( $\text{DMA}_{\text{g}}$ ) and particle phase ( $\text{DMA}_{\text{p}} + \text{DMAH}^+$ ) are shown. Figure 2 illustrates the sensitivity of organic salt predictions to  $\rho_{\text{L}}^{\circ}$  and  $\Delta pK_{\text{a}}$  values (ST 2<sub>AcOH</sub> with AcOH vs. ST 2<sub>pinic</sub> with pinic acid), to  $\sigma_{\text{m}}$  estimation (ST 2<sub>AcOH, $\sigma$</sub> ), and to  $\zeta_i$  estimation (ST 2<sub>AcOH, $\zeta$</sub> ). In all systems, most of the DMA mass is predicted to be in the particle phase as  $\text{DMAH}^+$ , with  $\text{DMAH}^+_{\text{AcOH},\zeta} > \text{DMAH}^+_{\text{pinic}} > \text{DMAH}^+_{\text{AcOH}} > \text{DMAH}^+_{\text{AcOH},\sigma}$ . The same is true for AcOH (ionic form) in ST 2<sub>AcOH</sub> and pinic acid (ionic form) in ST 2<sub>pinic</sub>. With ST 2<sub>AcOH</sub>,  $\sigma_{\text{m}} (=25.74 \text{ dyn cm}^{-1})$  is calculated as described in Sect. 2.2. This calculated value is similar to  $\sigma_{\text{m}}$  for a non-aqueous organic mixture when calculated according to  $\sigma_{\text{m}} = X_{\text{acid}}\sigma_{\text{acid}} + X_{\text{base}}\sigma_{\text{base}}$ . In cases where experimental data are available, measured

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$\sigma_m$  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 organic salt solutions, the presence of amines and  $\text{NH}_3$  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,  $\sigma_{\text{acid}} > \sigma_m \gg \sigma_{\text{base}}$ . Therefore, in ST 2<sub>AcOH, $\sigma$</sub>   $\sigma_m$  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  $p_j$ , and thus a decrease in predicted particle-phase DMA and AcOH, this effect is small compared to the predicted effects of varying activities,  $a_j (=X_j\zeta_j)$  as discussed below.

With ST 2<sub>AcOH</sub> and ST 2<sub>pinic</sub>,  $C$  is set according to Samson et al. (1999) for concentrated solutions with ionic strengths  $\leq 1.5$  M. Samson et al. (1999) found good agreement with experimental data when  $C$  was scaled linearly from 0.20 to 0.15, for solutions with ionic strengths from  $\sim 0$  to 1.5 M. The solutions considered here have much higher ionic strengths than 1.5 M. To potentially understand the effects of a more concentrated ionic solution,  $C$  was set = 0.10 in ST 2<sub>AcOH, $\zeta$</sub> . Decreasing  $C$  from 0.15 to 0.10 resulted in a predicted decrease in  $\zeta_j$  for the ionic species from  $\sim 67$  to  $\sim 17$ . The decrease in  $\zeta_{\text{ions}}$  results in a predicted increase in  $X_{j,\text{ions}}$ , and therefore a decrease in  $p_j$  (see Fig. 3). ST 2<sub>AcOH, $\zeta$</sub>  is predicted to have the greatest mass fraction of DMAH<sup>+</sup> and AcOH<sup>-</sup>, and thus the greatest extent of organic salt formation. Finally, ST 2<sub>pinic</sub> ( $\sigma_m = 26.84 \text{ dyn cm}^{-1}$ ,  $C = 0.15$ ) is predicted to have a greater mass fraction of DMAH<sup>+</sup> than ST 2<sub>AcOH</sub>. In this system, it is the much lower  $p_L^\circ$  of pinic acid than of acetic acid, and the greater  $\Delta pK_a$  for the organic salt of pinic acid ( $pK_{a,\text{DMA}} - pK_{a,\text{pinic}} = 6.00$ ) than that of acetic acid, that contribute to the greater extent of organic salt formation.

## 4 Discussion and conclusions

While amines have been detected in ambient accumulation mode (Silva and Prather, 2000; Denkenberger et al., 2007; Moffet et al., 2008) and nucleation mode (Mäkelä et al., 2001; Smith et al., 2008) particles, the mechanism(s) by which amines contribute to such particles has not been fully explored. As noted previously, the  $\rho_L^o$  values of low-MW amines found in the atmosphere are too high for such compounds to contribute to condensational growth of particles. This would be true to an even greater extent for the growth of newly formed particles, due to the Kelvin effect. Chamber studies have shown that oxidation of low-MW amines results in the formation of secondary organic aerosols (Pitts et al., 1978; Angelino et al., 2001; Murphy et al., 2007). Particle formation in the experiments of Angelino et al. (2001) and Murphy et al. (2007) was attributed to condensation of amine oxidation products, as well as the formation of aminium salts (w/nitric and/or sulfuric acids). Murphy et al. (2007) found that for aminium nitrate salts, amines generally partitioned back to the gas-phase as gas-phase amines were reacted away, leaving ammonium nitrate in the particle-phase; while for an aminium sulfate salt, methylamine appeared to displace ammonia, resulting in almost complete conversion to methylaminium sulfate.

In this work, the greater  $\Delta pK_a$  values of the aminium salts over the ammonium salts in ST 1 particles influenced the predicted extent to which each of the bases formed organic salts. When levels of  $\text{DMA}_g$  and  $\text{NH}_{3,g}$  were of the same order of magnitude, the formation of the dimethylaminium salt was predicted to be greater than the formation of the ammonium salt. In a more general consideration of the formation of aminium salts, when gas-phase amines and  $\text{NH}_3$  levels were of the same order of magnitude,  $K_H$  values of the amines and  $\Delta pK_a$  values of the organic salts significantly influenced the predicted extent of organic salt formation, with  $\Delta pK_a$  values having the greatest influence in the systems considered. In aqueous systems, a greater  $\Delta pK_a$  value indicates a greater degree of ionization, which would shift the equilibrium of the acids and bases to the particle phase. Even in non-aqueous systems  $\Delta pK_a$  values may give some insight

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into the degree of ionization. Yoshizawa et al. (2003) and Belieres and Angell (2007) showed that  $\Delta pK_a$  values of ionic liquids were approximately linearly correlated with excess boiling points. Yoshizawa et al. (2003) also found that ionic liquids with  $\Delta pK_a$  values  $>10$  exhibited properties indicating essentially complete proton transfer.

In dilute aqueous systems, ionic species have  $\zeta_i < 1$ , favoring the formation of organic salts as described above. In ST 2 particles, estimated  $\zeta_i$  values for organic ions were  $\gg 1$ . Estimated  $\zeta_i$  values for neutral organic acids and bases were 1 or slightly  $>1$  (with the exception of pinic acid,  $\zeta_{\text{pinic}} \approx 13$ ). In particles containing DMA and AcOH, varying  $a_i$  values (by varying  $\zeta_{\text{ions}}$ ) was predicted to have a greater effect on aminium salt formation than varying  $\sigma_m$ . The greatest extent of aminium salt formation was predicted when  $C=0.10$ , and the estimated  $\zeta_{\text{ions}}$  decreased from  $\sim 77$  to 17. The extent of organic salt formation in the systems considered here appears to be most sensitive to  $\Delta pK_a$  and  $\zeta_i$  values. However  $c_i$ ,  $K_{H,i}$ ,  $p_{L,i}^\circ$ , and  $\sigma_m$  values clearly play a role. Due to the lack of equilibrium data for the types of organic salt solutions considered here, and the limited modeling capabilities for highly concentrated solutions of neutral and ionized organics, these results 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 extent to which such salts contribute to the mass growth of existing aerosols and newly formed particles.

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**Table 1.** Chemical and physical property parameters for acids and bases considered.

	$\rho_L^\circ$ (atm) <sup>a</sup>	$K_H^a$ (M atm <sup>-1</sup> )	$pK_a$ (= -log $K_a$ )	$V_i^f$ (cm <sup>3</sup> mol <sup>-1</sup> )	$\sigma_i^f$ (dyn cm <sup>-1</sup> )	$V_c^c$ (cm <sup>3</sup> mol <sup>-1</sup> )
ammonia (NH <sub>3</sub> )	$9.81 \times 10^\circ$	$6.2 \times 10^1$	9.25 <sup>c</sup>	n/a	n/a	n/a
dimethylamine (DMA)	$2.04 \times 10^\circ$	$3.1 \times 10^1$	10.73 <sup>d</sup>	70.3	15.50	182.5
acetic acid (AcOH)	$2.09 \times 10^{-2}$	$8.8 \times 10^3$	4.76 <sup>c</sup>	56.1	31.90	171.0
pinic acid	$7.69 \times 10^{-10b}$	n/a	4.62 <sup>e</sup>	153.8	44.50	520.8 <sup>g</sup>
water	$3.09 \times 10^{-2}$	n/a	14.00 <sup>c</sup>	18.0	72.01	56.0

<sup>a</sup> Linstrom and Mallard (2005, <http://webbook.nist.gov/chemistry/>)

<sup>b</sup> Pankow and Asher (2008)

<sup>c</sup> CRC Handbook of Chemistry and Physics (Lide, 2008)

<sup>d</sup> Hall (1957, <http://www.webqc.org/pkaconstants.php>)

<sup>e</sup> SPARC (Hilal et al., 1995; <http://ibmlc2.chem.uga.edu/sparc/>)

<sup>f</sup> ACD/ChemSketch (2006)

<sup>g</sup> Constantinou and Gani (1994)

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**Table 2.** Relative amounts of dimethylamine (DMA) and ammonia ( $\text{NH}_3$ ) predicted in the particle phase, expressed as fractions of total base predicted in the particle phase, as a function of gas-phase DMA and  $\text{NH}_3$  levels (gas-phase acetic acid=100 ppt). Total fractions of DMA and  $\text{NH}_3$  are emboldened. Activity and curvature corrections have been neglected.

$f_i = n_{i,p}/n_{\text{totalbase},p}$	$\text{NH}_{3,g}=1000 \text{ ppt};$ $\text{DMA}_g=1 \text{ ppt}$	$\text{NH}_{3,g}=100 \text{ ppt};$ $\text{DMA}_g=1 \text{ ppt}$	$\text{NH}_{3,g}=1000 \text{ ppt};$ $\text{DMA}_g=10 \text{ ppt}$	$\text{NH}_{3,g}=100 \text{ ppt};$ $\text{DMA}_g=10 \text{ ppt}$
$f_{\text{DMAH}^+}$	0.015	0.133	0.133	0.605
$f_{\text{DMAp}}$	$\ll 0.001$	$\ll 0.001$	$\ll 0.001$	$\ll 0.001$
$f_{\text{DMAH}^+} + f_{\text{DMAp}}$	<b>0.015</b>	<b>0.133</b>	<b>0.133</b>	<b>0.605</b>
$f_{\text{NH}_4^+}$	0.983	0.866	0.866	0.394
$f_{\text{NH}_3}$	0.002	0.001	0.001	$\ll 0.001$
$f_{\text{NH}_4^+} + f_{\text{NH}_3}$	<b>0.985</b>	<b>0.867</b>	<b>0.867</b>	<b>0.394</b>

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**Table 3.** Observed low and high levels of aliphatic amines measured by Grönberg et al. (1992), and their Henry's Law ( $K_H$ ) and acid dissociation ( $K_a$ , as  $pK_a$ ) constants.

Amine	Low (ppt)	High (ppt)	$K_H$ (M atm <sup>-1</sup> ) <sup>a</sup>	$pK_a$ ( $= -\log K_a$ ) <sup>b</sup>
methylamine	2.4	29.4	36	10.62
dimethylamine	0.6	7.6	31	10.64
trimethylamine	1.5	39.1	9.6	9.76
diethylamine	0.4	11.5	39	10.98
triethylamine	trace	trace	29	9.25
total amines	4.9	87.6	n/a	n/a

Additional compounds included in system type 1 (ST 1) particles: ammonia (NH<sub>3</sub>), 10<sup>2</sup>–10<sup>4</sup> ppt (Seinfeld and Pandis, 1998),  $K_H = 61^a$ ,  $pK_a = 9.25^c$ ; and acetic acid (AcOH), 10<sup>2</sup>–10<sup>3</sup> ppt (Glasius et al., 2001; de Gouw et al., 2003),  $K_H = 8800^a$ ,  $pK_a = 4.76^c$ .

<sup>a</sup> Linstrom and Mallard (2005; <http://webbook.nist.gov/chemistry/>)

<sup>b</sup> Hall (1957, <http://www.webqc.org/pkaconstants.php>)

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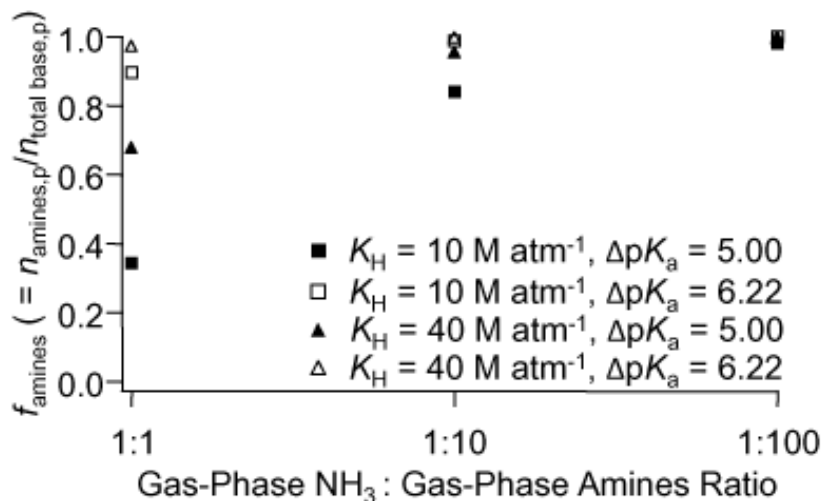
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## Contribution of organic salts to new particle growth

K. C. Barsanti et al.



**Fig. 1.** Fraction of amines predicted in the particle phase,  $f_{\text{amines}} (=n_{\text{amines,p}}/n_{\text{total base,p}})$ , for system type 1 (ST 1) particles (dilute aqueous) as a function of gas-phase  $\text{NH}_3$  and amine levels, and  $K_H$  and  $\Delta pK_a$  ( $pK_{\text{a,amine}} - pK_{\text{a,AcOH}}$ ) values.

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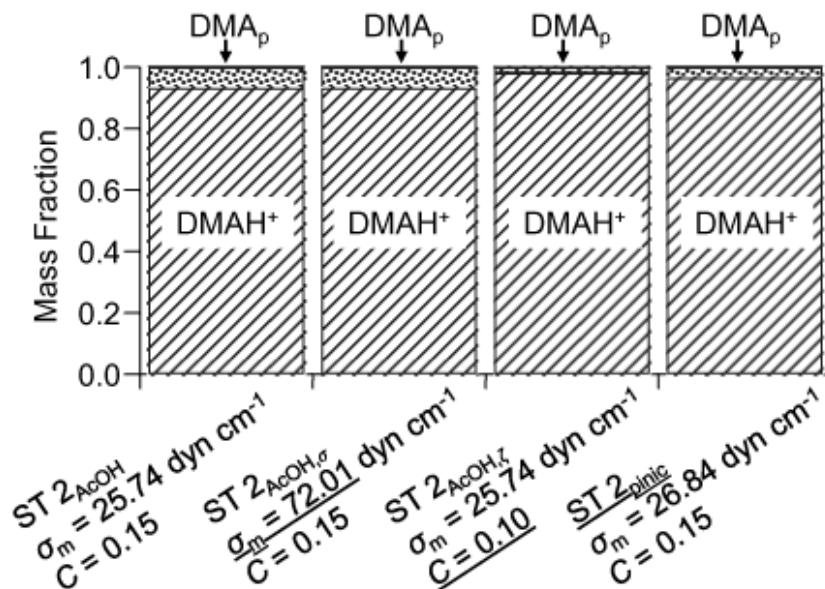
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**Fig. 2.** The predicted equilibrium distribution of dimethylamine between the gas (DMA<sub>g</sub>) and particle (DMA<sub>p</sub> and DMAH<sup>+</sup>) phases for system type 2 (ST 2) particles (aqueous particles  $w/X_{HA,initial}=0.25$  and  $X_{DMA,initial}=0.25$ ), shown as mass fraction in each phase; illustrating sensitivity to surface tension estimation (ST 2<sub>AcOH, $\sigma$</sub> ), activity coefficient estimation (ST 2<sub>AcOH, $\zeta$</sub> ), and vapor pressures/acid dissociation constants (ST 2<sub>pinic</sub>).

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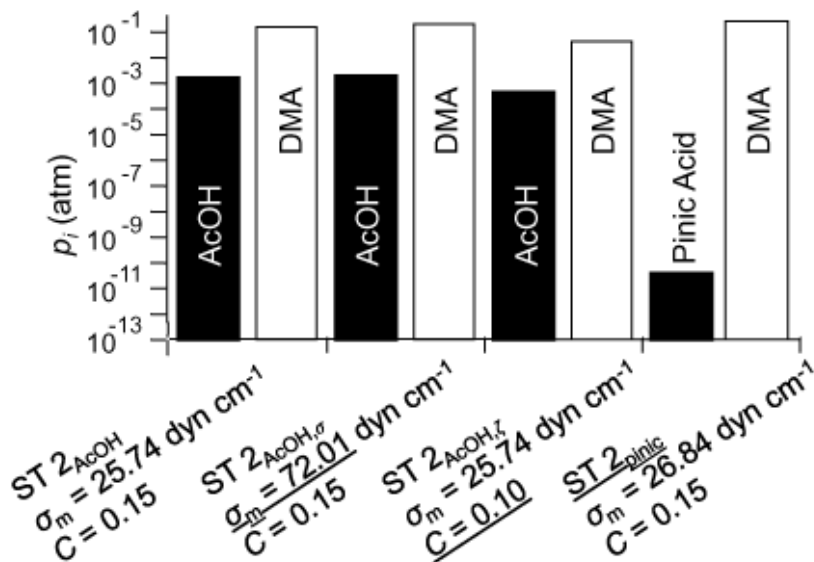
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**Fig. 3.** The predicted equilibrium amounts ( $p_i$ , atm) of gas phase acid (acetic, AcOH, and pinic) and base (dimethylamine, DMA) for system type 2 (ST 2) particles (aqueous particles  $w/X_{\text{HA,initial}}=0.25$  and  $X_{\text{DMA,initial}}=0.25$ ); illustrating sensitivity to surface tension estimation ( $ST_{2_{\text{AcOH},\sigma}}$ ), activity coefficient estimation ( $ST_{2_{\text{AcOH},\zeta}}$ ), and vapor pressures/acid dissociation constants ( $ST_{2_{\text{pinic}}}$ ).

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