

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.

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., Kerminen et al., 2005; Laaksonen 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 mean of 3–20% at 0.2% water supersaturation and of 5–50% at 1% water 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 predominantly, condensation (Weber et al., 1995). Correlations between sulfuric acid (H_2SO_4) concentrations and particle growth rates indicate that H_2SO_4 condensation can explain some, and occasionally all, observed particle growth (Stolzenburg et al., 2005). Growth rates in excess of H_2SO_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

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



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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_L°), one would not expect low-molecular weight amines and carboxylic acids to contribute to condensational growth of newly formed particles. For example, the p_L° 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 $1\text{--}10 \text{ nm h}^{-1}$ (Kulmala et al., 2004) lead to saturation vapor pressures (p_i) of $\sim 4 \times 10^{-16}$ atm for condensing compounds. Even condensation 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° 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_2O , H_2SO_4); reactions 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_3) neutralizes particles by reacting with H_2SO_4 and HNO_3 (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 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 ($p_{L,i}^\circ$) or Henry's Law constants ($K_{H,i}$); acid dissociation constants ($K_{a,i}$); and activity coefficients (mole scale, ζ_i). Additionally, the liquid molar-volume of each constituent (V_i) and the surface tension of the particle mixture (σ_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 acids, bases, and salts in each phase (where X_i is mole fraction):

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

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

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

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 $K_{H,i}$.

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 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, $p_{L,i}^\circ$ 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, $p_{L,i}^\circ$ 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 ζ_i for neutral species were calculated using UNIFAC (Fredenslund et al., 1977); values of ζ_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 ($< \sim 0.01 \text{ M}$). The second term is an empirical term and accounts for short range ion-ion interactions and solvation effects in more concentrated aqueous ionic solutions ($< \sim 0.5 \text{ M}$). A modified form of the Davies equation is given by Samson et al. (1999):

$$\ln = -Az_i^2 \left(\frac{\sqrt{I}}{1 + Ba_i\sqrt{I}} - \frac{CI}{\sqrt{1000}} \right) \quad (5)$$

where γ_i is the molal scale activity coefficient ($\zeta_i = \gamma_i (m_i MW_w)/(X_i * 1000)$, m_i is 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 ($A = 1.1744 \text{ kg}^{1/2} \text{ mol}^{-1/2}$, $B = 3.285 \times 10^9 \text{ kg}^{1/2} \text{ mol}^{-1/2} \text{ m}^{-1}$); I is ionic strength ($= \sum_i m_i z_i^2$, z is the charge on ion i); and a_i is the effective diameter of i ($= 3 \times 10^{-10} \text{ m}$). In the standard Davies equation, the empirical term takes the form bI , where $b = 0.2$ to 0.3 ; in the modified Davies equation of Samson et al. (1999), $C = 0.2$. 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 $X_i \rightarrow 1$, $\zeta_i \rightarrow 1$.

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 σ_i also were estimated using ACD/ChemSketch (2006). Values of σ_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 σ_m were calculated based on the initial 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. NH_3 in forming organic salts by considering partitioning of gas-phase amines, 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

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

	p_L° (atm) ^a	K_H^a (M atm ⁻¹)	pK_a (= -log K_a)	V_i^f (cm ³ mol ⁻¹)	σ_i^f (dyn cm ⁻¹)	V_c^c (cm ³ mol ⁻¹)
ammonia (NH ₃)	9.81×10^0	6.2×10^1	9.25 ^c	n/a	n/a	n/a
dimethylamine (DMA)	2.04×10^0	3.1×10^1	10.73 ^d	70.3	15.50	182.5
acetic acid (AcOH)	2.09×10^{-2}	8.8×10^3	4.76 ^c	56.1	31.90	171.0
pinic acid	7.69×10^{-10b}	n/a	4.62 ^e	153.8	44.50	520.8 ^g
water	3.09×10^{-2}	n/a	14.00 ^c	18.0	72.01	56.0

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

^b Pankow and Asher (2008)

^c CRC Handbook of Chemistry and Physics (Lide, 2008)

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

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

^f ACD/ChemSketch (2006)

^g Constantinou and Gani (1994)

Table 2. Relative amounts of dimethylamine (DMA) and ammonia (NH₃) predicted in the particle phase, expressed as fractions of total base predicted in the particle phase, as a function of gas-phase DMA and NH₃ levels (gas-phase acetic acid=100 ppt). Total fractions of DMA and NH₃ are emboldened. Activity and curvature corrections have been neglected.

$f_i = n_{i,p}/n_{\text{totalbase},p}$	NH _{3,g} =1000 ppt; DMA _g =1 ppt	NH _{3,g} =100 ppt; DMA _g =1 ppt	NH _{3,g} =100 ppt; DMA _g =10 ppt
f_{DMAH^+}	0.015	0.133	0.605
f_{DMA_p}	$\ll 0.001$	$\ll 0.001$	$\ll 0.001$
$f_{\text{DMAH}^+} + f_{\text{DMA}_p}$	0.015	0.133	0.605
$f_{\text{NH}_4^+}$	0.983	0.866	0.394
f_{NH_3}	0.002	0.001	$\ll 0.001$
$f_{\text{NH}_4^+} + f_{\text{NH}_3}$	0.985	0.867	0.394

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 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)

For an aqueous nanometer-sized particle, the relative amounts of particle-phase DMA and NH₃ 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 σ_m of dilute aqueous DMA solutions (Hyvärinen et al., 2004) are less than σ_m of dilute aqueous NH₃ solutions (Paul and Chandra, 2005). Therefore, while the absolute amount of organic salts formed likely will change as a function of surface tension (and therefore particle size), the relative importance of amines vs. NH₃ may not change. 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 NH₃. The results suggest that when the level of gas-phase DMA (DMA_g) is within an order of magnitude (or greater) of gas-phase NH₃ (NH_{3,g}), DMA (DMA_p+DMAH⁺, where DMA_p≪DMAH⁺) will be more abundant in the particle

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 ⁻¹) ^a	pK_a ($=-\log K_a$) ^b
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 one (ST 1) particles: ammonia (NH₃), 10²–10⁴ ppt (Seinfeld and Pandis, 1998), $K_H=61$ ^a, $pK_a=9.25$ ^c; and acetic acid (AcOH), 10²–10³ ppt (Glasius et al., 2001; de Gouw et al., 2003), $K_H=8800$ ^a, $pK_a=4.76$ ^c

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

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

^c CRC Handbook of Chemistry and Physics (Lide, 2008)

phase than NH₃ (NH_{3,p}+NH₄⁺, where NH_{3,p}≪NH₄⁺). This is due to DMA and NH₃ having Henry's Law constants of similar magnitude, 31 and 62 M atm⁻¹ respectively; but DMA having significantly greater basicity than NH₃, with ΔpK_a ($pK_{a,base} - pK_{a,acid}$)=5.88 for DMA and AcOH and $\Delta pK_a=4.49$ for NH₃ 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 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 ΔpK_a) values must be considered.

Table 3 lists the low and high levels of five aliphatic amines measured by Grönberg et al. (1992), 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 of possible values for ambient amines. For these general considerations, the fraction of amines in the particle phase ($f_{amines}=n_{amines,p}/n_{totalbase,p}$, where n is mols) is shown in Fig. 1, as a function of gas-phase NH₃ and amine levels, and K_H and ΔpK_a values ($pK_{a,amine} - pK_{a,AcOH}$). From Fig. 1 it can be seen that when the level of gas-phase amines is on the order of gas-phase NH₃, K_H and ΔpK_a values play a significant role in determining the amount of amines vs. the amount of NH₃ in the particle phase. While DMA was predicted to be more abundant than NH₃ in the particle phase when the levels of DMA_g were within an order of magnitude of NH_{3,g}, amines with $K_H=10$ and $\Delta pK_a=5.00$ are predicted to be less abundant in the particle phase even with equivalent levels of amines and NH₃ in the gas phase. For these particular K_H and ΔpK_a values, at the 10:1, 1:1 and 1:10 gas-phase ratios, increasing ΔpK_a is predicted to play a greater role than increasing K_H in promoting organic salt formation; while at the 100:1 gas-phase ratio, increasing

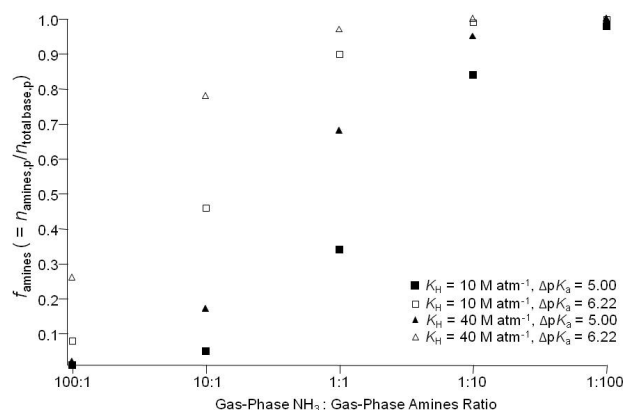


Fig. 1. Fraction of amines predicted in the particle phase, f_{amines} ($=n_{amines,p}/n_{totalbase,p}$), for system type one (ST 1) particles (dilute aqueous) as a function of gas-phase NH₃ and amine levels, and K_H and ΔpK_a ($pK_{a,amine} - pK_{a,AcOH}$) values.

K_H is predicted to play a greater role. Also from Fig. 1 it can be seen that when amines greatly exceed NH₃ in the gas phase (or when NH₃ greatly exceeds DMA), K_H and ΔpK_a values become less important in predicting the relative contribution of amines vs. NH₃ to organic salt formation. 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)

Figure 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_L° and ΔpK_a values (organic salt formation w/AcOH, ST 2_{AcOH}, vs. w/pinic acid, ST 2_{pinic}), to σ_m

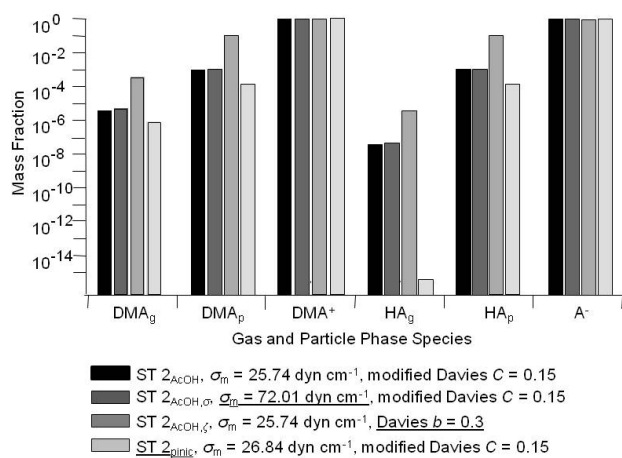


Fig. 2. The predicted equilibrium distribution of dimethylamine, acetic acid, and pinic acid between the gas (DMA_g , HA_g) and particle (DMA_p , DMAH^+ , HA_p , A^-) phases for system type two (ST 2) particles (aqueous particles w/ $X_{\text{HA,initial}}=X_{\text{DMA,initial}}=0.25$), shown as mass fraction in each phase. The relative mass fractions illustrate the sensitivity of predictions to surface tension estimation ($\text{ST } 2_{\text{AcOH},\sigma}$), activity coefficient estimation ($\text{ST } 2_{\text{AcOH},\zeta}$), and vapor pressures/acid dissociation constants ($\text{ST } 2_{\text{pinic}}$).

estimation ($\text{ST } 2_{\text{AcOH},\sigma}$), and to ζ estimation ($\text{ST } 2_{\text{AcOH},\zeta}$). Most of the DMA mass is predicted to be in the particle phase as DMAH^+ , with $\text{DMAH}^+_{\text{pinic}} > \text{DMAH}^+_{\text{AcOH}} > \text{DMAH}^+_{\text{AcOH},\sigma} > \text{DMAH}^+_{\text{AcOH},\zeta}$ (see DMA_g , Fig. 2). The same is true for the acids, AcOH (ionic form) in $\text{ST } 2_{\text{AcOH}}$ and pinic acid (ionic form) in $\text{ST } 2_{\text{pinic}}$ (see HA_g , Fig. 2). Regarding sensitivity to p_L° and ΔpK_a values, $\text{ST } 2_{\text{pinic}}$ ($\sigma_m=26.84 \text{ dyn cm}^{-1}$) is predicted to have a greater mass fraction of DMAH^+ than $\text{ST } 2_{\text{AcOH}}$ ($\sigma_m=25.74 \text{ dyn cm}^{-1}$). While the estimated surface tension is slightly greater in the system with pinic acid and $\zeta_{\text{pinic}} > \zeta_{\text{acetic}}$, it is the much lower p_L° of pinic acid than that of acetic acid, and the greater ΔpK_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.

Regarding sensitivity to surface tension, for $\text{ST } 2_{\text{AcOH}}$ (initial composition: $X_{\text{water}}=0.5$, $X_{\text{acid}}=X_{\text{base}}=0.25$), σ_m is calculated as described in Sect. 2.2. That calculated value is similar to σ_m for a *non-aqueous* organic mixture when calculated using a simple binary approach, $\sigma_m=X_{\text{acid}}\sigma_{\text{acid}}+X_{\text{base}}\sigma_{\text{base}}$. Experimental data have shown that measured σ_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 (Mmerekı 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 $\text{ST } 2_{\text{AcOH},\sigma}$ σ_m was set= σ_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 ($=X_i \zeta_i$), discussed below.

Regarding sensitivity to activity coefficients, the standard and modified Davies equations are typically valid for solutions with ionic strengths $<0.5 \text{ M}$. 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 C in 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 $\text{ST } 2_{\text{AcOH}}$, ζ_{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 in calculated ζ_{ions} values is significant, $\sim 10^0$ to 10^2 , and therefore estimation of ζ_{ions} has the greatest affect on the predicted extent of organic salt formation. As the calculated ζ_{ions} values increase, the predicted amounts of DMAH^+ decrease, increasing DMA_p and DMA_g . However, even when $\zeta_{\text{ions}} \approx 10^2$ ($b=0.3$), the mass fraction of $\text{DMAH}^+ \approx 0.9$ ($\text{ST } 2_{\text{AcOH},\zeta}$).

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 p_L° 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 ΔpK_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 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 NH_3 levels were of the same order of magnitude, K_H values of the amines and ΔpK_a values of the organic salts significantly influenced the predicted extent of organic salt formation, with ΔpK_a values having the greatest influence in the systems considered. In aqueous systems, a greater ΔpK_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 ΔpK_a values may give some insight into the degree of ionization. Yoshizawa et al. (2003) and Belieres and Angell (2007) showed that ΔpK_a values of ionic liquids were approximately linearly correlated with excess boiling points. Yoshizawa et al. (2003) also found that ionic liquids with ΔpK_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 ζ_i values for organic ions ranged from 10^0 to 10^2 , as a function of the chosen empirical parameter in the Davies equation. Estimated ζ_i values for neutral organic acids and bases were ≈ 1 (with the exception of pinic acid, $\zeta_{\text{pinic}} \approx 10^1$). In particles containing DMA and AcOH, varying ζ_{ions} was predicted to have a greater effect on aminium salt formation than varying σ_m . The extent of organic salt formation in the systems considered here appears to be most sensitive to ΔpK_a and ζ_i values. However c_i , $K_{H,i}$, $p_{L,i}^0$, and σ_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, the 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 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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