



**Inorganic salts
interact with organic
di-acids**

G. Drozd et al.

Inorganic salts interact with organic di-acids in sub-micron particles to form material with low hygroscopicity and volatility

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

Volatility and hygroscopicity are two key properties of organic aerosol components, and both are strongly related to chemical identity. Here we show that inorganic-organic component interactions typically not considered in atmospheric models may strongly affect aerosol volatility and hygroscopicity. In particular, bi-dentate binding of di-carboxylic acids (DCA) to soluble inorganic ions can lead to very strongly bound metal-organic complexes with largely undetermined hygroscopicity and volatility. These reactions profoundly impact particle hygroscopicity, transforming hygroscopic components into irreversibly non-hygroscopic material. While the hygroscopicities of pure salts, DCA, and DCA salts are known, the hygroscopicity of internal mixtures of hygroscopic salts and DCA, as they are typically found in the atmosphere, has not been fully characterized. We have studied the volatility of pure, dry organic salt particles and the hygroscopicity of internal mixtures of oxalic acid (OxA, the dominant DCA in the atmosphere) and a number of salts, both mono- and di-valent. The formation of very low volatility organic salts was confirmed, with minimal evaporation of oxalate salt particles below 75 °C. Dramatic increases in the CCN activation diameter for particles with divalent salts (e.g. CaCl₂) and relatively small particle mass fractions of OxA indicate that standard volume additivity rules for hygroscopicity do not apply. Thus small organic compounds with high O : C are capable of forming low volatility and very low hygroscopicity particles. Given current knowledge of the formation mechanisms of OxA and M-Ox salts, surface enrichment of insoluble M-Ox salts is expected. The resulting formation of an insoluble coating of metal-oxalate salts can explain low particle hygroscopicities. The formation of particles with a hard coating could offer an alternative explanation for observations of glass-like particles with very low viscosity.

Inorganic salts interact with organic di-acids

G. Drozd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



1 Introduction

The ubiquity of dicarboxylic acids (DCA) is well documented both in urban and rural terrestrial aerosol and marine aerosol (Warneck, 2003; Wang et al., 2006; Wang and Kawamura, 2006; Tan et al., 2010; Sempéré and Kawamura, 1996; Pavuluri et al., 2010; Ma et al., 2013; Kundu et al., 2010; Kawamura et al., 1996, 2007; Gierlus et al., 2012; Altieri et al., 2008). A recent study of marine aerosol from around the globe found that DCA contribute on average ~ 15% to total marine organic aerosol (OA) mass (Fu et al., 2013; Myriokefalitakis et al., 2011) DCA are commonly associated with aqueous processing of water soluble organics (Ervens et al., 2011; Tan et al., 2010) and hence readily affect aerosol–water interactions. Oxalic acid (OxA) is typically the dominant DCA found in aerosol (Neusüss et al., 2000). It was shown to contribute more than 50% on average of the total mass of marine DCA, and mineral dust is often enriched in OxA (Sullivan et al., 2009; Fu et al., 2013). High oxidation states and the ability to strongly interact with inorganic compounds (especially crustal/marine salts) make the effects of DCA on aerosol composition and physical properties unique and complex. However the impact of such interactions on particles' properties are not well understood. In this study we focus on DCA interactions with inorganic salts and their impacts on hygroscopicity and volatility.

Reactions of OxA with deliquescent salts of monovalent and divalent cations represent an important class of DCA : salt interactions in atmospheric aerosols. Monovalent cations are typically a major inorganic constituent of atmospheric aerosol, in particular Na^+ (e.g. from NaCl) and $(\text{NH}_4)^+$ (e.g from $(\text{NH}_4)_2\text{SO}_4$) Divalent cations may be a significant component of sea-salt (e.g. MgCl_2 , CaCl_2) and mineral dust (e.g. CaCO_3). Seawater aerosol may typically contain 10 wt% divalent salts (Pratt et al., 2010), while dust aerosol is more variable with at least 5–10 wt% CaCO_3 , or more (Kumar et al., 2009; Sullivan et al., 2009). OxA may react with both mono- and di-valent cations to form low volatility complexes, but the metal valency will largely determine OxA : metal effects on hygroscopicity. While monovalent ions (Na^+ , NH_4^+ , etc.) react with DCA to

Inorganic salts interact with organic di-acids

G. Drozd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Inorganic salts
interact with organic
di-acids**

G. Drozd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Finally, separate particle populations containing DCA and divalent metals in an external mixture may combine via coagulation to form internal mixtures (Ma and He, 2012). Thus there are multiple formation pathways for particles consisting of soluble di/poly-valent salts and DCA, and the hygroscopicity of these particles will depend on both the amount of DCA : metal complexation and the final particle morphology (i.e. potential surface enrichment of insoluble complexes).

Accurately describing gas-particle partitioning and predicting atmospheric aerosol loading requires knowledge of how low-volatility salts contribute to particle growth and alter the overall volatility of aerosol particles (Lee et al., 2012). Low-volatility atmospheric species have special importance since they participate in aerosol particle growth, in particular the growth of very small, freshly-nucleated particles (Kulmala et al., 2004; Pierce et al., 2011; Riipinen et al., 2012). Aerosol particles smaller than 50 nm in diameter are expected to contain compounds with equilibrium vapor pressures as low as 10^{-8} – 10^{-7} Pa (Pierce et al., 2011). Such low vapor pressures can be achieved by organic salt formation via acid-base reactions (Riipinen et al., 2012; Barsanti et al., 2009). For example, OxA has a high vapor pressure ($\sim 10^{-2}$ Pa), but the majority of atmospheric OxA resides in the particle phase due to oxalate formation (Ervens et al., 2011 and references therein). The formation of organic salts is also a reactive sink of particle-phase organics, enhancing gas phase uptake (Pierce et al., 2011). Recently, the formation of low-volatility organic salts has been observed under various atmospheric conditions in reactions of organic acids with mineral salts (Laskin et al., 2012), ammonium (Martinelango et al., 2007; Dinar et al., 2008; Ortiz-Montalvo et al., 2012) and amines (Sorooshian et al., 2008; Smith et al., 2010).

Recent field studies, performed both in urban and remote environments, have pointed out the existence of very low-volatility (non-volatile even at temperatures as high as 280 °C) organics in submicron aerosol particles (Wehner et al., 2002; Ehn et al., 2007; Backman et al., 2010; Häkkinen et al., 2012). Häkkinen et al. (2012) observed a positive correlation between low-volatile aerosol material, atmospheric particulate organics, and organic nitrates at a boreal forest site in Central Finland, owing to the

**Inorganic salts
interact with organic
di-acids**

G. Drozd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



presence of low-volatility organonitrates or organic salts. Since the contribution of sea salt (or other mineral salts) in submicron particles at continental forest sites far from the sea is minor (Saarikoski et al., 2005), ammonium or aminium salts are likely main contributors to the growth of aerosol particles, even at sub-20 nm sizes (Barsanti et al., 2009; Smith et al., 2010). However, at marine sites or other mineral rich areas the contribution of organic salts from mineral-salt:organic-acid reactions may have a significant effect on aerosol chemical properties and further cloud processing (Furukawa and Takahashi, 2011; Laskin et al., 2012). These results emphasize the fact that atmospheric species, both organic and inorganic, can undergo drastic changes when they react with each other and these changes can alter the chemical and physical properties of particles.

This study addresses the major effects of DCA-cation interactions on two key aerosol properties, hygroscopicity and volatility. Towards understanding these effects, internally mixed particles were created by exposing several metal-chloride salts to gas-phase OxA. The hygroscopicity and volatility of the resulting particles was then studied. From the results we assess the applicability of the standard volume additivity rules for hygroscopicity (κ -Köhler theory) and aerosol partitioning of organics that may bind to metals in terms of surface processes and unaccounted inorganic-organic interactions.

2 Methods

2.1 Experimental

2.1.1 Aerosol generation

For hygroscopicity measurements, salt-oxalate aerosols were generated by deposition of gas-phase oxalic acid onto dry, inorganic aerosol. Salt particles were generated from solutions of CaCl_2 (Sigma Aldrich), MgCl_2 (Sigma Aldrich), ZnCl_2 (Sigma Aldrich), NaCl (Sigma Aldrich), and $\text{Na}_2\text{C}_2\text{O}_4\text{H}_2$ (Sigma Aldrich). In addition to solutions of each

through a diffusion drier charged with silica bead desiccant prior to heating. The mean number concentrations and geometric mean diameters of the generated particles (oxalic acid, NaOx and CaOx) measured with a SMPS (during oxalic acid and NaOx experiments SMPS by TSI, during CaOx experiment SMPS by Grimm Technologies) before introducing the aerosol to the TPD Aerosol-CIMS are presented in Table 1.

2.1.2 Temperature Programmed Desorption Aerosol-CIMS

TPD Aerosol-CIMS (Temperature Programmed Desorption Aerosol-Chemical Ionization Mass Spectrometer) consists of a quadrupole mass spectrometer coupled with a heated volatilization flow tube inlet (McNeill et al., 2007). Compared to more traditional instruments which measure aerosol volatility by detecting change in aerosol particle diameter upon heating (Philippin et al., 2004; Wehner et al., 2005; Ehn et al., 2007), TPD Aerosol-CIMS detects changes in volatilized aerosol organics in the gas phase via CIMS. In the heating region the aerosol stream flows through a PFA tube (o. d. 1.27 cm, length 23 cm) wrapped with a heating tape (VWR). Diluted aerosol flow of 1.8 L min⁻¹ from the total flow of 5–6 L min⁻¹ enters the heating tube giving the aerosol a residence time of less than a second in the tube. The temperature in the heated region is controlled by a temperature controller (Staco Energy Products Co.) and monitored using a thermocouple. The aerosol (gas-particle mixture) is then introduced to an ionizer where the gas-phase analyte molecules (i.e., oxalic acid) react with I⁻ reagent ion to form clusters (see details in Sareen et al., 2010). Ion clusters are guided from atmospheric pressure to ultrahigh vacuum ($\sim 10^{-8}$ Torr) using differential pumping and the masses (mass-to-charge ratio, m/z) of these clusters are determined using a quadrupole mass spectrometer. Aerosol evaporation is observed as an increase in signal when the temperature in the vaporization flow tube (VFT) is increased. In this study mean temperatures at the VFT centerline were used in the data analysis. Linear correspondence between the temperature of the flow tube external wall and the actual VFT temperature was determined in the range of 25–114 °C. For a more detailed description of the instrument used, see Sareen et al. (2010).

30660

ACPD

13, 30653–30685, 2013

Inorganic salts interact with organic di-acids

G. Drozd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Inorganic salts
interact with organic
di-acids**

G. Drozd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



When investigating the volatility of oxalate salts (NaOx, CaOx), the heating temperature was increased step-wise using mean inlet temperatures from 25 °C to 180 °C (altogether at 8–9 temperatures). Signal response for a given molecular cluster to temperature change was rapid. It took around 30 to 90 min to stabilize per temperature setting. The studied oxalate salts were observed as clusters of oxalic acid and I⁻ in the TPD Aerosol-CIMS. Detecting organic salts in the CIMS as their corresponding acids has been observed before (McNeill et al., 2007). It is known that gas phase oxalic acid can thermally decompose at sufficiently high temperatures (~ 100 °C) forming formic acid and CO₂ (Higgins et al., 1997). This was taken into account when performing oxalate salt experiments; instead of tracing only oxalic acid (217 ± 0.5 amu, I⁻ · C₂H₂O₄) also formic acid (173 ± 0.5 amu, I⁻ · CH₂O₂) was traced and the total oxalate signal was taken as the sum of these two signals (e.g. Fig. 4). The observed oxalate signal was 1–10 % of the mass spectrometer signal of the reagent ion, which was ~ 100 kcps.

The calibration of the TPD Aerosol-CIMS was done with pure oxalic acid aerosol observed as a cluster of I⁻ (for more about the calibration and other data analysis, see the Heat of vaporization and Volatility of oxalate salts sections). All of the TPD Aerosol-CIMS experiments were performed at relative humidities below 10 % in order to keep the contribution of water negligible (Saleh et al., 2010; Cappa et al., 2007). This was done by drying the particles using silica gel dryer after particle generation. Due to minor contamination inside the ionization regime and/or in the tubing, a constant background of oxalate was always present. Before every experiment the background was determined and removed from the observed oxalate signal in the data analysis.

2.2 Data-analysis/modeling

2.2.1 Hygroscopicity and CCN activity

Hygroscopicities of aerosol mixtures were compared using κ , a single parameter representation of CCN activity (Petters and Kreidenweis, 2007),

$$\kappa = \frac{4A^3}{27D_d^3 \ln^2(1 + s_c)} \quad (1)$$

where s_c is the supersaturation required for a given particle of dry diameter, D_d , to activate. A is a constant-temperature parameter expressing particle curvature effects on vapor pressure

$$A = \frac{4\sigma_{s/a} M_w}{RT\rho_w} \quad (2)$$

where $\sigma_{s/a}$ is the solution surface tension at the point of activation, M_w is the molecular mass of water, R is the universal gas constant, T is the solution temperature, and ρ_w is the density of water. The surface tension of water, 0.072 J m^{-2} , was used for all κ calculations.

For mixtures of soluble component species, κ can be approximated as a summation of its volume-fraction-weighted terms:

$$\kappa = \sum_i \kappa_i \varepsilon_i \quad (3)$$

where κ_i and ε_i are the individual component hygroscopicities and volume fractions, respectively. Using the volume of oxalic deposition onto the inorganic aerosol, and literature and measured values of pure substance hygroscopicities, or κ values, (Tables 1 and 2) were calculated taking into account the conversion of oxalic acid and inorganic

salts to their respective oxalate salts. The calculated values for κ reflect a theoretical range of hygroscopicities that can arise from reaction and bulk mixture effects alone. Deviations from this range of values suggests additional compositional effects not accounted for by mixing alone.

5 2.2.2 Enthalpy of vaporization

The effective enthalpies of vaporization of the aerosol constituents (ΔH_{vap} , kJ mol^{-1}) can be determined using TPD Aerosol-CIMS, by applying Clausius–Clapeyron equation as follows:

$$\ln \left(\frac{\text{signal}(T_2)}{\text{signal}(T_1)} \right) = -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (4)$$

10 where R is gas constant, T is mean temperature of the gas in the flow tube and the mean observed signal $\text{signal}(T)$ is proportional to the effective vapor pressure of the studied aerosol species. ΔH_{vap} depends on temperature, however, it can be approximated as a constant in relatively narrow temperature ranges. Hence, Eq. (4) can be considered a linear equation and ΔH_{vap} can be determined from the slope of the curve
15 fitted to the experimental data using least-square method that takes into account known covariance. The covariance of each data point (mean signal at temperature T) was the standard deviation of the aerosol-CIMS signal squared. The curvature (Kelvin) effect on vapor pressure was found to be insignificant in the calculation of ΔH_{vap} . According to calculations ($\frac{2\sigma M}{\rho_l r_p}$ vs. $\Delta H_{\text{vap,CIMS}}$, where σ , M and ρ_l are surface tension, 72 mNm^{-1} ,
20 molar mass, $126.07 \text{ g mol}^{-1}$, and liquid density, 1.653 g cm^{-3} , respectively) the influence of Kelvin effect on the ΔH_{vap} is minor (below 1% with r_p of 20 nm). Equation (4) also assumes compounds do not react during the heating process.

Inorganic salts interact with organic di-acids

G. Drozd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



3 Results and discussion

CCN activity expressed by log-log plots of d_p vs. s_c for sodium-dominated particles are shown in Fig. 2. Pure salt particles are shown in solid curves, while salt particles with OxA deposited are shown with dashed curves. For reference, pure sodium oxalate and ammonium sulfate are shown by the thick-dashed red line, and the thick black line, respectively. Following an analysis similar to that of Sullivan et al. (2009) we can calculate intrinsic κ values, κ_{intr} (i.e. hygroscopicity if the material is completely soluble), to aid the interpretation of observed hygroscopicities,

$$\kappa_{\text{intr}} = \frac{\nu \rho_s M_w}{\rho_w M_s} \quad (5)$$

where ρ_s is the density and M_s the molecular weight of the material, ρ_w is the density and M_w the molecular weight of water, and ν is the number of ions for complete dissociation of the solute. These values are shown in Table 2 for monovalent salts and their hydrates (densities from CRC handbook). While our measurements for the pure monovalent chloride aerosols (with no oxalate) yield κ values that are consistent with previously measured values, measurements for monovalent salts containing oxalate are similar to those of salt-hydrates, even after drying. This is consistent with the findings of Ma et al. (2013), which suggest the persistence of hydrates under dry conditions, without heating in addition to drying. Addition of oxalate to sodium (monovalent) dominated salt particles has only a modest effect, due to their high solubility. From the results of Sullivan et al. (2009) large increases in hygroscopicity may result from mixing small amounts of highly soluble material to lower solubility material that has a high intrinsic hygroscopicity. Added water solubilizes the low solubility core and induces non-linear response in mixing. The orange points in Fig. 1 show mixtures of NaCl with the other main component in sea salt, MgCl_2 . The two mixtures are 8 : 1 and 1 : 1 NaCl/ MgCl_2 , and it is clear that deposition of OxA to particles with greater di-valent salt content creates significantly less hygroscopic particles. The measured hygroscopicities for these mixtures in fact agree well with the calculated κ_{intr} , as might be expected for particles

30664

ACPD

13, 30653–30685, 2013

Inorganic salts
interact with organic
di-acids

G. Drozd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



with dominant (8 : 1 NaCl/MgCl₂) and significant (1 : 1 NaCl/MgCl₂) amounts of highly soluble NaCl.

The CCN measurements for particles dominated by di-valent salts, both pure and after OxA deposition, are shown in Fig. 3. In all cases, deposition of OxA incurs a very large decrease in hygroscopicity to the salt particles, as indicated by substantial increases of the critical diameter at a given supersaturation. For the pure divalent salt particles, the measured κ values are much lower than the pure salts, but agree closely with the salt-hydrates (Table 3). As for the monovalent salts, this is reasonable because fully removing water from the deliquesced salt particles can require heating in addition to low humidity (Ma et al., 2013).

The s_c vs. d_p curves for the mixtures of di-valent salts and OxA (Fig. 3) are not linear over the full range of measurements. For example, the d_p for CaCl₂ + OxA at an s_c of ~ 0.4 is roughly 30 nm below the linear trend of the κ values at high s_c . This itself suggests surface effects are at play, because hygroscopicities seem to be affected by the surface-area:volume ratio of the particle.

Calculating the κ values of the final mixtures present after OxA deposition is slightly complicated by the volatility of co-formed HCl upon reaction of the salt with oxalic acid. As has been shown by Laskin et al. (2012), drying mixtures of diacids (malonic, etc.) with chloride salts can cause HCl to be expelled from the particle, as evidenced by a 30 % loss of Cl upon reaction. Given that particles in our study were prepared in a similar manner to the Laskin et al. (2012) approach, chloride depletion is likely to occur for the divalent salts as has been observed for NaCl. Cl depletion must be taken into account when estimating the fraction of OxA actually deposited to our salt particles, because we measure the particle diameter after evaporation of HCl would have occurred. Thus, the final particle volume can be expressed as the sum of the component volume fractions multiplied by their respective molar volumes. Assuming

Inorganic salts interact with organic di-acids

G. Drozd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



negligible changes to the individual component molar during reaction,

$$V_{\text{final}} = V_{\text{init}} - V_{\text{react}} + V_{\text{prod}} \quad (6)$$

$$\frac{V_{\text{react}}}{V_{\text{init}}} = f_{\text{react}} = \frac{GF - 1}{(\beta_{\text{tot}} - 1)} \quad (7)$$

5 where V_{final} is the measured particle volume after OxA deposition and any chemistry that occurs after OxA deposition, V_{init} is the initial, pure-salt particle volume, V_{react} is the volume of the pure salt that reacts, V_{prod} is the volume of the reaction products, f_{react} is the fraction of oxalic acid reacted, GF is the ratio of the final-to-initial particle diameter, and β_{tot} is the sum of the molar volume of the products divided by molar volume of the pure salt.

The volatility of HCl gives rise to two limiting cases in which HCl is treated as completely remaining in the particle and one in which HCl completely evaporates from the particle. The first case is given by:

$$\kappa_{\text{max}} = \frac{(1 - f_{\text{react}})\kappa_{\text{Salt}} + f_{\text{react}}(\beta_{\text{M-Ox}}\kappa_{\text{M-Ox}} + \beta_{\text{HCl}}\kappa_{\text{HCl}})}{(1 - f_{\text{react}}) + f_{\text{react}}(\beta_{\text{M-Ox}} + \beta_{\text{HCl}})} \quad (8)$$

15 and the second case (complete HCl evaporation) is given by

$$\kappa_{\text{min}} = \frac{(1 - f'_{\text{react}})\kappa_{\text{Salt}} + f'_{\text{react}}\beta_{\text{M-Ox}}\kappa_{\text{M-Ox}}}{(1 - f'_{\text{react}}) + f'_{\text{react}}\beta_{\text{M-Ox}}} \quad (9)$$

where now

$$f'_{\text{react}} = \frac{(GF - 1)}{(\beta_{\text{M-Ox}} - 1)} \quad (10)$$

20 and $\beta_{\text{M-Ox}}$ is the stoichiometry-weighted ($n_{\text{M-Ox}}/n_{\text{salt}}$) ratio of the molar volume of M-Ox to the initial pure-salt molar volume.

The assumption that the final particle volume was measured after complete reaction and evaporation of HCl results in the lowest prediction of the final particle hygroscopicity, because the particle would then contain the maximum possible fraction of insoluble, low-hygroscopicity material. These results are listed in Table 4. The complete reaction is in fact not likely to occur, as the Cl : Na ratios for particles with initial 1 : 1 molar ratio of acid to salt observed by Laskin et al. (2012) never reached zero. While the observed particle hygroscopicities (after OxA deposition) for divalent salts are low (0.02–0.05), the lowest predicted hygroscopicity is 0.30 for MgCl₂. The measured κ values are close to the values expected/measured for the pure M-Ox compounds, which have fairly high κ_{intr} that are not realized due to their low solubilities (Sullivan et al., 2009).

The discrepancies between the measured and predicted particle hygroscopicities can be attributed, at least in part, to particle morphologies with inhomogeneous composition, such as a coating. A possible explanation is the formation of an insoluble M-Ox coating at the particle surface. This is supported by the similar κ values for our salt particles with OxA deposition and the pure M-Ox particles measured by Sullivan et al. (2009). Recently, species present at the particle surface, such as surfactants, have been shown to strongly affect CCN activation (Sareen et al., 2013). Though M-Ox compounds may reduce particle surface tensions to as low as 32 mN m⁻¹ (Wu and Nancollas, 1999), we find good agreement between our measured and calculated κ values for the NaCl : MgCl₂ mixtures using a surface tension of 72 mN m⁻¹. Thus a coating of the insoluble M-Ox may create a particle that, in terms of CCN activation, behaves as if the particle were composed entirely of the insoluble M-Ox salt. This potential scenario is also supported by the fact that evolution of HCl from the particle, which leaves behind insoluble M-Ox, must occur at the particle surface. Finally, a recent study has shown incomplete mixing may commonly occur in ambient salt particles, with divalent salts enriched at the particle surface (Ault et al., 2013). Thus, organic coatings, which may lead to formation of insoluble organic salts, may be prevalent in the atmosphere.

Inorganic salts interact with organic di-acids

G. Drozd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



3.1 Volatility of oxalate salts

The TPD Aerosol-CIMS was calibrated using oxalic acid with well-known ΔH_{vap} (83 kJ mol^{-1} at $T = 190^\circ\text{C}$, Yaws, 2013). In order to determine the ΔH_{vap} of oxalic acid aerosol, the average oxalic acid gas phase signal at three different temperatures (mean inlet temperatures $25, 39, 56^\circ\text{C}$) was divided with the average signal at room temperature (25°C) and its logarithm was plotted against the inverse mean inlet temperature (Fig. 5, upper panel). This way the Clausius–Clapeyron equation could be directly applied (Eq. 4) and ΔH_{vap} could be estimated from the slope of the calibration curve. In the temperature range of $25\text{--}56^\circ\text{C}$ we obtained ΔH_{vap} of $(85 \pm 12) \text{ kJ mol}^{-1}$ for oxalic acid (Table 1), comparable to the literature value for ΔH_{vap} of oxalic acid (95 kJ mol^{-1}) (Yaws, 2003). A residence time of one second may not be sufficient to fully equilibrate the aerosol (Riipinen et al., 2010). However, high particle concentrations and small the particle sizes yield shorter equilibrium times, and in our case particles concentrations are high and particles relatively small, compared to the conditions of Riipinen et al. (2010).

CaOx volatility measurements were performed along with CCN measurements by coupling the TPD Aerosol-CIMS with the CFTSGC system (Fig. 1). NaOx experiments were performed separately. Data for the first NaOx experiment (NaOx(1)) is shown in Fig. 4; signal noise was small and the background oxalate level low. A slight, stable signal increase above background signal was observed at room temperature for NaOx(1), possibly due to changes in CIMS ionization or residual gas phase oxalate. All other measurements had oxalate signals at the same level as the background (difference around 100 Hz) indicating minimal evaporation below 75°C .

The evaporation curves obtained from the oxalate salt measurements are illustrated in Fig. 5; the calibration curve of oxalic acid is also shown for comparison. The NaOx particles were generated by atomizing an aqueous solution of sodium oxalate, so the CaOx particles, made by depositing Ox on CaCl_2 , seem to behave as if made from pure CaOx. The volatility of the M-Ox salts was very different from that of pure OxA

Inorganic salts interact with organic di-acids

G. Drozd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Inorganic salts
interact with organic
di-acids**

G. Drozd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



aerosol. The onset temperature of evaporation (clear increase in signal) for both NaOx and CaOx was found to be around 75 °C, whereas OxA was volatile at room temperature (Table 4 and Fig. 5). Hence, the oxalate salt particles were significantly less volatile compared to pure oxalic acid aerosol. In other words, the energy needed for the vaporization of oxalates, ΔH_{vap} , was very large at temperatures below 75 °C, whilst ΔH_{vap} was (85 ± 12) kJ mol⁻¹ for pure OxA. Similar to our study, high onset temperatures of evaporation have been observed also with other atmospheric organic constituents (Tritscher et al., 2011; Meyer et al., 2009). Tritscher et al. (2011) reported onset evaporation temperature of around 70 °C for citric acid and both Tritscher et al. (2011) and Meyer et al. (2009) observed onset evaporation temperature of around 50 °C for secondary organic aerosol from α -pinene oxidation.

At temperatures above 75 °C, where volatilization of oxalates was observed to be significant, the vapor pressure of oxalates did not follow a strictly exponential dependence with T (Fig. 5), in contrast to OxA aerosol (Riipinen et al., 2006, 2007). It is possible that the thermal decomposition of OxA causes a convolution of two separate signals with slightly different onset temperatures. The complexity of the thermal decomposition was not further studied, because it is not atmospherically relevant. However, we acknowledge that it has some influence on our results at higher temperatures and may be important in thermodynamic experiments. In order to estimate the energy needed for the vaporization of oxalate salts at temperatures > 75 °C, the ΔH_{vap} in this temperature range was determined using (see the lower panel of Fig. 5 for the example linear fit). The average of the obtained ΔH_{vap} values for oxalate salts was (72 ± 12) kJ mol⁻¹ (Table 1). As discussed above, this value should be taken only as an estimate. TPD Aerosol-CIMS results show that, in the case of CaOx and NaOx, OxA/oxalate is sequestered as very low-volatility organic salt compounds.

4 Conclusions and atmospheric implications

Deposition of OxA to sub-micron particles containing di-valent salts creates very low hygroscopicity material. Dramatic increases in the CCN activation diameter, up to 50 nm, for relatively small particle mass fractions of OxA (10–20 %) with divalent salts (e.g. CaCl_2) indicate that standard volume additivity rules for hygroscopicity do not apply. High oxidation state, soluble organic species can strongly decrease hygroscopicity in particles dominated by divalent salts. Given current knowledge of the formation mechanisms of OxA and M-Ox salts, surface enrichment of insoluble M-Ox salts is expected, explaining the greater than stoichiometric effects of M-Ox salts on particle hygroscopicity. An analogous situation does not occur for particles dominated by monovalent salts (NaCl), as κ values from the standard κ -calculation for a mixture (Eq. 3) agree with our measurements. A threshold of soluble material is likely met in particles dominated by monovalent salts, such that overall solubility is high enough to reach ideal behavior. Particles containing oxalate salts, whether pure or formed by OxA deposition to pure salt particles, have very low volatility, indicated by a 75 °C “onset-temperature” for detection of OxA using TPD Aerosol-CIMS. A coating of insoluble material such as CaOx could result in particles that are hard enough to exhibit bounce on particle impactors and, combined with the low volatility of these salts, may also affect mass transfer properties (evaporation/uptake) of such coated particles. The formation of an insoluble and hard coating of organic salts, supported by the discrepancy between our calculated and observed hygroscopicities, could thus appear in experimental observations (mass transfer limitations and bounce factor) as a glassy, highly viscous state. Because of the potential implications for partitioning/volatility, uptake coefficients, evaporation, and hygroscopicity, the *irreversible* transformation of volatile, soluble, and high oxidation-state organic material into non-volatile material may be important in models of organic compound partitioning in the atmosphere.

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Inorganic salts interact with organic di-acids

G. Drozd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Inorganic salts
interact with organic
di-acids**

G. Drozd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Inorganic salts
interact with organic
di-acids**

G. Drozd et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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**Inorganic salts
interact with organic
di-acids**

G. Drozd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Inorganic salts
interact with organic
di-acids**

G. Drozd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Inorganic salts
interact with organic
di-acids**

G. Drozd et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Inorganic salts interact with organic di-acids

G. Drozd et al.

Table 1. Physical properties of the generated particle size distribution – mean geometric size and mean concentrations of the particles during the TPD aerosol-CIMS experiments are presented. In addition parameters describing the evaporation of these particles are shown (onset temperature for evaporation and ΔH_{vap} of oxalate at different temperature ranges with a number of data points used in the linear fits in parentheses). Experiments were performed using oxalic acid aerosol, sodium oxalate (NaOx) and calcium oxalate (CaOx).

Aerosol	Physical properties measured with SMPS		Evaporation properties measured with TPD Aerosol-CIMS		
	Mean geometric diameter (nm)	Mean total particle number concentration (10^4 cm^{-3})	Onset T ($^{\circ}\text{C}$)	ΔH_{vap} ($< 75^{\circ}\text{C}$)	ΔH_{vap} ($> 75^{\circ}\text{C}$)
Oxalic acid	41	1.1	25	85 ± 12 (3)	–
NaOx (1)	75	6.6	75	–	64 ± 8 (4)
NaOx (2)	76	8.2	75	–	64 ± 5 (4)
CaOx	100	39.1	75	–	87 ± 36 (3)

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Inorganic salts interact with organic di-acids

G. Drozd et al.

Table 2. κ values for monovalent salts. κ_{intr} calculated using Eq. (5). The densities are from CRC handbook, except for $\text{Na}_2\text{Ox}-(4-\text{H}_2\text{O})$, which was assigned a density of 1.52 g cm^{-3} .

Aerosol Species	κ_{intr}	κ_{meas}	κ_{lit}
$(\text{NH}_4)_2\text{SO}_4$	0.73	0.61	0.61 ^a
NaCl	1.34	1.05	1.28
Na_2Ox	0.95	0.4	–
$\text{Na}_2\text{Ox}-(4-\text{H}_2\text{O})$	0.4	0.4	–
OxA	1.14	0.21	0.2–0.5 ^{a, b}
$\text{OxA}-(2-\text{H}_2\text{O})$	0.71	0.21	0.2–0.5 ^{a, b}

^a Sullivan (2009).

^b Petters (2009).

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


Inorganic salts interact with organic di-acids

G. Drozd et al.

Table 3. Solubilities (-sol), intrinsic κ values (κ_{intr}), and measured κ values (κ_{meas}) for di-valent metal salts and their hydrates (Cl-Hyd). κ_{intr} were calculated using Eq. (5) with densities from the CRC handbook.

Aerosol Species	Cl-sol (g L ⁻¹)	Cl- κ_{intr}	(Cl-Hyd)- κ_{intr}	Cl- κ_{meas}
Zn	4080	1.16	0.71	0.75
Ca	813	1.05	0.68	0.64
Mg	560	1.32	0.42	0.47

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Inorganic salts interact with organic di-acids

G. Drozd et al.

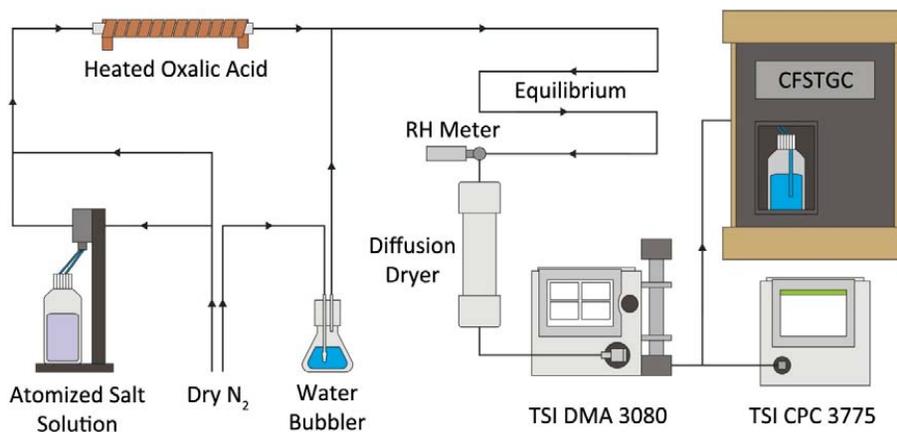
Table 4. κ values for salts and salt mixtures with OxA deposition. Equations (8) and (9) are used to calculate κ_{calc} . Our measured component κ values are used for the individual components' κ_i , and a GF of 1.2 was used.

Aerosol Composition	κ_{calc}	κ_{meas}
NaCl + OxA	0.81	0.68
8 : 1: NaCl : MgCl ₂ + OxA	0.76–0.81	0.81
1 : 1: NaCl : MgCl ₂ + OxA	0.31–0.57	0.46
MgCl ₂ + OxA	0.3	0.05
CaCl ₂ + OxA	0.46	0.02
ZnCl ₂ + OxA	0.51	0.02

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


**Inorganic salts
interact with organic
di-acids**

G. Drozd et al.

**Fig. 1.** A schematic diagram of the experimental setup.

Inorganic salts interact with organic di-acids

G. Drozd et al.

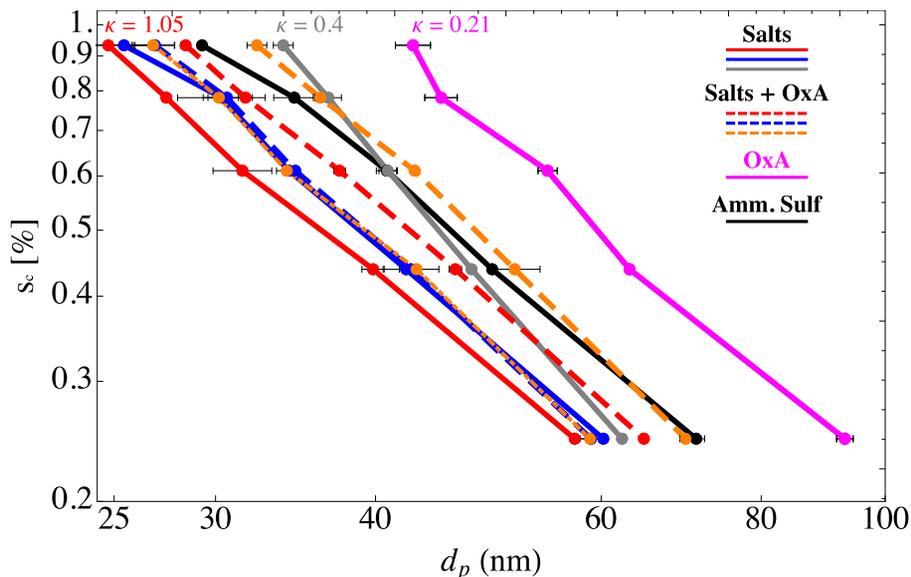


Fig. 2. Critical supersaturation, s_c , of monovalent salt particles as a function particle diameter. Results for inorganic salts without OxA deposition are shown by solid lines: NaCl (red), Instant Ocean (blue), Na_2Ox (grey). The corresponding salts with OxA deposition are dashed lines with the same color. The orange, thick-dashed and thin-dashed lines are for the 1 : 1 and 8 : 1 mixtures of NaCl : MgCl_2 with OxA deposition, respectively. Pure OxA and ammonium sulfate are shown in solid magenta, and black lines, respectively. κ values are shown for NaCl (red), Na_2Ox (grey), and OxA (magenta).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Inorganic salts interact with organic di-acids

G. Drozd et al.

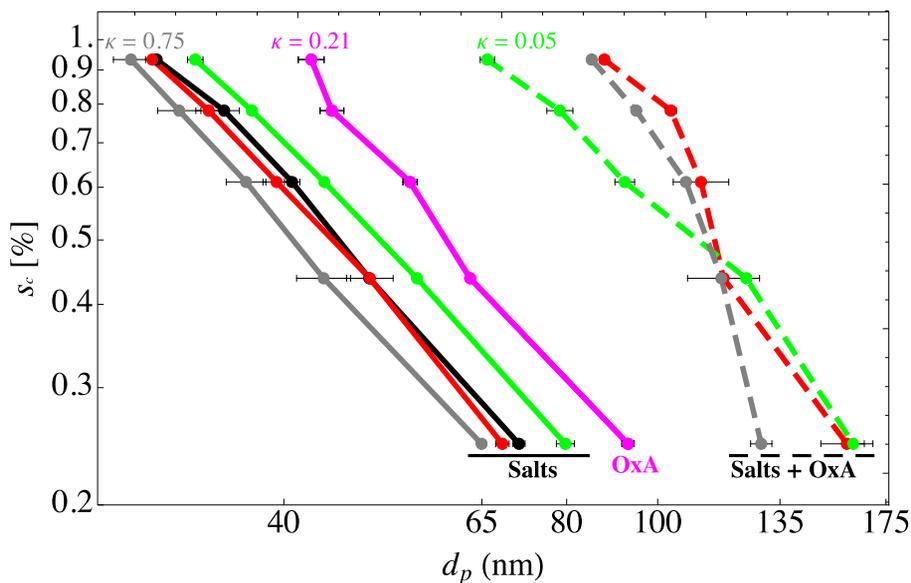


Fig. 3. Critical supersaturation, s_c , of divalent salt particles as a function particle diameter. Inorganic salts without OxA deposition are shown by solid lines: ZnCl₂ (gray), CaCl₂ (red), MgCl₂ (green). The corresponding salts with OxA deposition are dashed lines with the same color. Pure OxA and ammonium sulfate are shown in solid magenta, and black lines, respectively. κ values are shown for ZnCl₂ (gray), OxA (magenta), and MgCl₂ + OxA (green).

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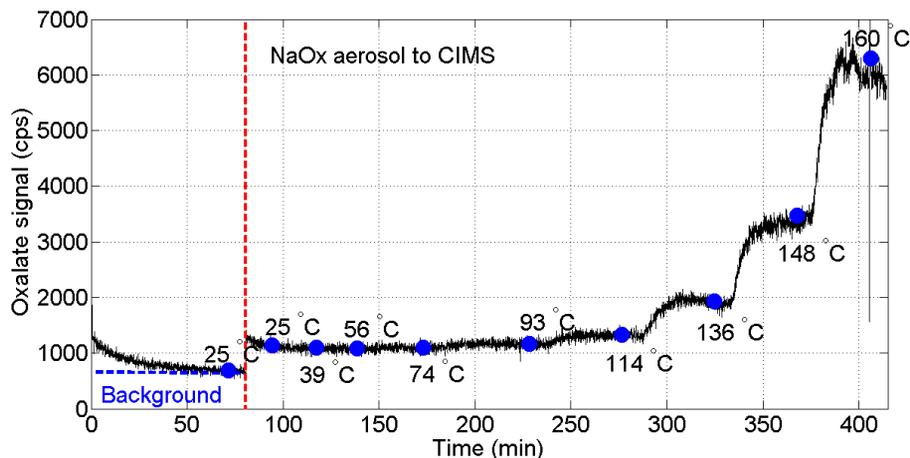


Fig. 4. Volatility of NaOx aerosol with TPD Aerosol-CIMS (NaOx (1)). The detected oxalate signal when aerosol was heated stepwise from room temperature to 160 °C as a function of time (minutes from the beginning of the experiment) is illustrated in the figure (black solid line). Also the average oxalate signal at different temperatures is plotted (blue dots). The average background oxalate signal was subtracted from the oxalate signal for further analysis.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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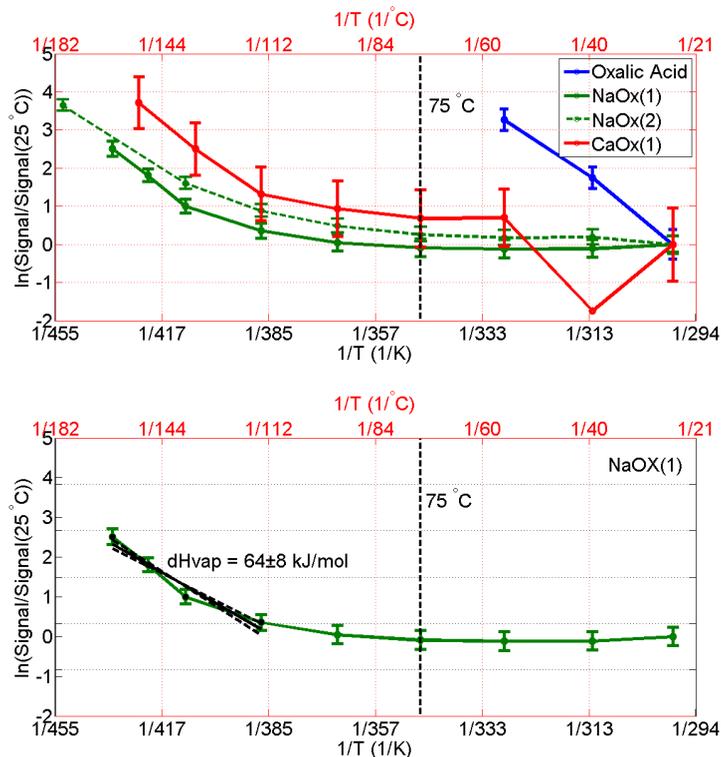


Fig. 5. Evaporation of oxalate particles observed with the TPD aerosol-CIMS – natural logarithm of the oxalate signal normalized with the signal at room temperature as a function of inverse mean inlet temperature. Oxalic acid calibration curve (blue), two independent experiments with NaOx (green) and CaOx along CCN experiment (red) are illustrated in the upper panel. Also the approximate onset temperature of evaporation of oxalate salts is marked (75 °C). In the lower panel the estimation of the ΔH_{vap} by fitting the data points to Clausius–Clapeyron equation (Eq. 4) above this temperature is shown for NaOx particles (NaOx (1)). Error bars illustrate the standard deviation of the signal from the mean signal.