Effect of different organic salts on ammonia volatilization in ammonium nitrate

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Abstract. The ammonium salts and organic salts are the important components of atmospheric aerosols. The reaction between the two salts will cause the release of NH₃, hence, affecting the budget of NH₃ in the atmosphere. Furthermore, the equilibrium partitioning of NH₃ in the gas and particle phases plays a key role in the evolution of chemical composition and size of fine atmospheric particles. In this work, the chemical composition evolution processes of mixed particles consisting of four different organic acid salts (sodium oxalate (SO), sodium malonate (SM), sodium succinate (SS), sodium pyruvate (SP)) with ammonium nitrate (AN) were measured by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). The release of NH₃ were gained by monitoring the changes in the absorbance of NH₄⁺ in mixed organic acid salts/AN particles under 70% relative humidity (RH). After 127 minutes, the remaining ammonium content in the four mixed aerosols was 84.2%, 71.6%, 57.1%, and 28.7% for SO, SM, SS, and SP mixed with AN, respectively, which is lower than that in pure AN aerosol (97%). This study may help to further understand the conversion process between organic salts and AN in the atmosphere, as well as the NH₃ cycles in the atmosphere.

1. Introduction
Atmospheric aerosols have an increasing impact on human health, the earth's radiation balance, climate and visibility, etc. Therefore, further studies on the properties and composition of atmospheric aerosols have attracted more attention [1]. In recent years, the frequent outbreaks of heavy haze are mainly caused by the increase of particle concentration caused by gas-particle transformation and gas-particle distribution. The volatility of matter is a key factor of gas-particle transformation and distribution. Volatility is one of the most important and basic characteristics of atmospheric aerosols, which represents the gas-particle distribution balance between the gas phase and particle phase, therefore, affects the lifetime of aerosol particles in the atmosphere.

Ammonia (NH₃) is a very important alkaline component in the atmosphere, which has direct and indirect effects on regional fine particles, acid rain and eutrophication and other environmental problems [2], and plays an important role in atmospheric chemistry. In addition, NH₃ can neutralize H₂SO₄ and HNO₃ in the atmosphere and form (NH₄)₂SO₄, NH₄HSO₄ and NH₄NO₃ [3]. Global ammonia emissions have more than doubled since the industrial era, mainly due to the effects of agricultural intensification. Therefore, it is particularly important to study the release of NH₃ and the gas-particle equilibrium with NH₄⁺ in the atmosphere.

Low molecular weight carboxylic acids occupy a large proportion in atmospheric organic aerosols, Oxalic acid is the most abundant dicarboxylic acid in atmospheric aerosols, followed by malonic acid and succinic acid [4,5]. Dicarboxylic acids with low molecular weight, such as malonic acid, succinic acid
and glutaric acid, are also important semi-volatile organic compounds \[6\]. Due to their low vapor pressure, they are easy to be concentrated on the surface of aerosol particles, thus affecting the formation and growth of aerosol particles \[7\]. Field measurement found that a large part of the water-soluble organic salt in atmospheric environmental particles is converted from water-soluble organic acid \[8\]. Kerminen et al. \[9\] showed that oxalate, malonate, succinate and methanesulfonate accounted for 20-30% of the chloride loss in sea salt aerosols in northern Finland.

Previous studies \[10\] have fully explored the effect of dicarboxylate salts (\(\text{Na}_2\text{C}_2\text{O}_4\), \(\text{CH}_2\text{(COONa)}_2\) and \((\text{CH}_2\text{COONa})_2\)) on the hygroscopicity of ammonium sulfate aerosols with different organo-inorganic mixing ratios during a dehydration and hydration cycle. The results showed that the interaction between water soluble organic salts and \((\text{NH}_4)_2\text{SO}_4\) in aqueous aerosols may impact the redistribution of \(\text{NH}_3\) between condensed phase and gas phase, thereby altering the composition, physicochemical properties and related chemical processes of aerosols.

Sodium pyruvate was found to interact with ammonium sulfate leading to the release of volatile pyruvic acid and ammonia \[11\]. This reaction was accompanied by a loss of water, leading to the formation of sodium sulfate crystals. The observed continuous chemical reactions and the resulting chemical composition evolution are attributed to the gas particle evaporation.

Water-soluble organic salts are an important part of atmospheric aerosols. However, the effect of water-soluble organic salts on ammonia volatilization in ammonium nitrate is still unclear. Therefore, it is of great significance to conduct further research on organic salts and inorganic ammonium salts in atmospheric particles. In this study, several common organic carboxylates (sodium oxalate, sodium malonate, sodium succinate, sodium pyruvate) were selected to discuss the composition changes caused by the reaction of different organic carboxylates with ammonium nitrate and the difference in ammonia volatilization.

2. Methods and Materials

2.1 Sample preparation

0.1M aqueous solutions were prepared of SO/AN, SM/AN, SS/AN, SP/AN with organic/inorganic ratios (OIR) of 1:2, 1:2, 1:2 and 1:1. The purity of all reagents is higher than 99%. The aerosol particles with the size of 1-10 µm were nebulized from solutions and deposited on the ZnSe substrate.

2.2 ATR-FTIR measurement

The experimental setup used in this study has been described in detail in previous studies \[12,13\]. It mainly consists of sample chamber, spectrometer, humidity control system and aerosol generator. The angle of the incident infrared beam is 45°, and 12 total internal reflections occur at the ZnSe/air interface. The spectra are collected by an FTIR spectrometer (Nicolet Magna-IR 560A) equipped with a mercury cadmium telluride type A (MCT/A) detector. The spectrum is obtained by scanning 32 times with a resolution of 4 cm\(^{-1}\), and the wave number range is 650 cm\(^{-1}\) to 4000 cm\(^{-1}\). RH in the sample chamber is changed by adjusting the ratio of dry and wet N\(_2\). All experiments are performed at room temperature.

2.3 Data processing

This experiment uses OMNIC (Nicolet Co.) and Origin software (Origin 8.5) to process spectral data. The collected experimental spectra is subtracted from gaseous water absorption to obtain the original spectra. Then, the areas of the corresponding characteristic bands are calculated to quantify the species contents. The normalized ammonium content is quantified by integrating the band range from 3120 to 3020 cm\(^{-1}\).
3. Results and Discussion

3.1 Infrared spectra of pure AN

The infrared spectra of AN aerosols in the dehumidification and the dehumidification processes are shown in Figure 1. As shown in the figure 1(a), on dehydration, the peak of NO$_3^-$ ($\nu_2$-NO$_3^-$) located at 829 cm$^{-1}$ gradually weakened and shifted to 831 cm$^{-1}$, meanwhile, the feature peak of NH$_4^+$ ($\nu_4$-NH$_4^+$) shifted from 1448 cm$^{-1}$ to 1421 cm$^{-1}$. These peak changes occurred in the range of 32.6%-22% RH, indicating the efflorescence relative humidity (ERH) of AN at 32.6%-22% RH. The characteristic peaks of AN undergo reverse shift at 59.6% RH during the humidification process, showing the deliquescence relative humidity (DRH) at 59.6% RH \cite{14}.

![Fig. 1. FTIR spectra of pure AN droplets with the RH (a) on dehumidifying (b) on humidifying.](image)

3.2 Infrared spectra of mixed organic salt/AN particles at constant RH

Figure 2 shows the time-dependent infrared spectra of four organic salts (SO, SM, SS, SP) mixed with AN in stoichiometric ratio at a constant RH of 70%. Figure 2(a) presents the infrared spectra of SO/AN mixed aerosol with OIR of 1:2. The two absorption peaks at 3436 cm$^{-1}$ and 1630 cm$^{-1}$ are the stretching vibration peak ($\nu$-OH) and the bending vibration peak ($\delta$-OH) of OH, respectively, and the broad band at 2800-3400 cm$^{-1}$ is attributed to the stretching vibration absorption peak of NH$_4^+$ ($\nu$-NH$_4^+$). The band at 1338 cm$^{-1}$ is the characteristic peak of SO, and the absorption peaks located at 1425 cm$^{-1}$ and 829 cm$^{-1}$ are attributed to the characteristic of bending vibration of ammonium ($\nu_2$-NH$_4^+$) and out-of-plane bending vibration of NO$_3^-$ ($\nu_2$-NO$_3^-$), respectively. It can be observed that hardly any infrared absorption peaks change of SO/AN mixed aerosol after the reaction has proceeded for 127 min with a bit decrease of the band at 2850 cm$^{-1}$.

For SM/AN mixed aerosol with an OIR of 1:2, the infrared spectra of mixed aerosols in Figure 2(b) shows that a new peak of $\nu$-(COOH) appears at 1715 cm$^{-1}$ and increases with the passage of experiment time. At the same time, the strength of the $\nu_2$-COO$^-$ located at 1572 cm$^{-1}$ is weakened and gradually shifts to 1592 cm$^{-1}$ with the increase of time, which corresponds to the features of monosodium malonate,
indicating that the content of SM is decreasing continuously and monosodium malonate \(^{[10]}\) is formed. These changes show the following reaction:

\[
\text{NaOOCCH}_2\text{COONa} + \text{NH}_4\text{NO}_3 \rightarrow \text{HOOCCH}_2\text{COONa} + \text{NaNO}_3 + \text{NH}_3 \uparrow
\]  \hspace{1cm} (1)

The formed \(\text{NH}_3\) gas releases to atmosphere, leading to \(\text{NH}_4^+\) content loss in particles. Figure 2(c) is the infrared spectra of SS/AN mixed aerosols with OIR=1:2 with the time exposed to 70% RH. The two absorption peaks at 1552 cm\(^{-1}\) and 1390 cm\(^{-1}\) are assigned to asymmetric stretching vibration (\(\nu_{as-\text{COO}}\)) and symmetric stretching vibration (\(\nu_{s-\text{COO}}\)) of \(\text{COO}^-\), respectively. The bands at 1355 cm\(^{-1}\) and 829 cm\(^{-1}\) are the characteristic peaks of asymmetric stretching vibration of \(\text{NO}_3^-\) (\(\nu_{as-\text{NO}_3^-}\)) and out-of-plane bending vibration (\(\nu_{2-\text{NO}_3^-}\)), respectively. The infrared absorption peak at 1176 cm\(^{-1}\) is due to the out-of-plane bending vibration of the methylene group (\(\gamma-\text{CH}_2\)). As the reaction proceeds, a new peak (\(\nu-\text{COOH}\)) at 1715 cm\(^{-1}\) appears and the gradual increase in peak-height, which indicates an increase in succinic acid content. The weakening of the peak at 1552 cm\(^{-1}\) means the depletion of SS. These phenomena imply that SS reacts with AN to form succinic acid, SN and \(\text{NH}_3\), the equation is as follows:

\[
\text{NaOOC(CH}_2\text{)_2COONa} + \text{NH}_4\text{NO}_3 \rightarrow \text{HOOC(CH}_2\text{)_2COOH} + \text{NaNO}_3 + \text{NH}_3 \uparrow
\]  \hspace{1cm} (2)

The infrared spectra of the internally mixed aerosol of SP/AN with an OIR of 1:1 is shown in Figure 2(d). The peak at 1708 cm\(^{-1}\) rises to asymmetric stretching vibration of \(\text{C}=\text{O}\) (\(\nu_{as-\text{C}=\text{O}}\)), the two bands at 1618 cm\(^{-1}\) and 1394 cm\(^{-1}\) are owing to the symmetric stretching vibration of \(\text{COO}^-\) (\(\nu_{s-\text{COO}}\)). The absorption peak at 1354 cm\(^{-1}\) comes from the symmetrical bending vibration of the methyl group (\(\delta-\text{CH}_3\)), the band at 1178 cm\(^{-1}\) is attributed to the stretching vibration of \(\text{C}-\text{C}\) (\(\nu_{-\text{C}-\text{C}}\)) and bending vibration of \(\text{COO}^-\) (\(\gamma-\text{COO}^-\)). The absorption peaks at 1708 cm\(^{-1}\), 1618 cm\(^{-1}\), 1394 cm\(^{-1}\), 1354 cm\(^{-1}\) and 1178 cm\(^{-1}\) become gradual weaker with the reaction, indicating the depletion of SP in the mixed particles. It reveals that the reaction between SP and AN in internally mixed SP/AN aerosols at 70% RH lead to pyruvic acid (PA), SN and \(\text{NH}_3\), and pyruvic acid formation. \(\text{NH}_3\) can volatilize from liquid particles into the gas \(^{[11]}\), the process is shown in equation (3):

\[
\text{CH}_3\text{COCOONa} + \text{NH}_4\text{NO}_3 \rightarrow \text{CH}_3\text{COCOOH} \uparrow + \text{NaNO}_3 + \text{NH}_3 \uparrow
\]  \hspace{1cm} (3)
3.3 Understanding the ammonia Volatility for different organic salts/AN aerosols

In order to understand the effects of different organic salts on ammonia volatility in AN, the integrated area of NH$_4^+$ feature bands at 3060 cm$^{-1}$ ($\nu_4$-NH$_4^+$ stretching mode) in different mixtures is used to characterize the ammonium content. Figure 3 describes the change trend of ammonium content under the condition of RH of 70% for pure AN and four salt/AN aerosols mixing with stoichiometric ratio. It can be found that the NH$_3$ release increase owing to addition of organic salts compared to pure AN particle. When the time is 127 minutes, the remained ammonium contents are 97%, 84.2%, 71.6%, 57.1% and 28.7% corresponding to pure AN, SO/AN, SM/AN, SS/AN and SP/AN, respectively. The order should be related to the hygroscopicity of produced compounds and volatility in final particles.

Fig. 2. FTIR spectra of different organic salts/AN aerosols with stoichiometric ratio at RH of 70% (a) SO/AN (b) SM/AN (c) SS/AN (d) SP/AN.

Fig. 3. The change curve of ammonium content in organic salt/AN mixed aerosol with time at 70% RH.
4. Conclusions
By analyzing the infrared spectra, it was found that and the addition of organic salts changes the composition of the aerosol, resulting in more ammonia volatilization than pure AN at 70% RH. The chemical reaction takes place in the mixed aerosol of SO/AN, SM/AN and SS/AN, the volatilization of NH$_3$ and the formation of low hygroscopic dicarboxylic acid are the driving forces of the reaction between dicarboxylic acid and AN. The formation and volatilization of pyruvate acid and NH$_3$ leads to the reduction of product in SP/AN aerosol droplets, which promotes the forward reaction and further promotes the volatilization of NH$_3$.

Usually, it is thought that ammonia is converted to ammonium in the air. However, the current work appears to reveal a reverse particle-gas partitioning process. The present results indicate that the NH$_3$ repartition into air is dependent upon the organic acid, which can significantly influence the air quality and compound cycles in atmosphere.

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