Hygroscopicity measurement of sodium carbonate, β-alanine and internally mixed β-alanine/Na₂CO₃ particles by ATR-FTIR

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ABSTRACT

Water-uptakes of pure sodium carbonate (Na₂CO₃), pure β-alanine and internally mixed β-alanine/Na₂CO₃ aerosol particles with different mole ratios are first monitored using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) technique. For pure Na₂CO₃ aerosol particles, combining the absorptions at 877 and 1422 cm⁻¹ with abrupt water loss shows the efflorescence relative humidity (ERH) of 62.9%–51.9%. Upon humidifying, solid Na₂CO₃ firstly absorbs water to form Na₂CO₃·H₂O crystal at 72.0% RH and then deliquesces at 84.5% RH (DRH). As for pure β-alanine particles, the crystallization takes place in the range of 42.4%–33.2% RH and becomes droplets at ~88.2% RH. When β-alanine is mixed with Na₂CO₃ at various mole ratios, it shows no efflorescence of Na₂CO₃ when β-alanine to Na₂CO₃ mole ratio (OIR) is 2:1. For 1:1 and 1:2 β-alanine/Na₂CO₃ aerosols, the ERHs of Na₂CO₃ are 51.8%–42.3% and 57.1%–42.3%, respectively. While β-alanine crystal appears from 62.7% RH for 2:1 and 59.4% RH for both 1:1 and 1:2 particles and lasts to driest state. On hydration, the DRH is 44.7%–75.2% for Na₂CO₃ with the OIR of 1:1 and 44.7%–69.0% for 1:2 mixture, and those of β-alanine are 74.8% for 2:1 mixture and 68.9% for two others. After the first dehumidification–humidification, all the water contents decrease despite of constituent fraction. And at ~92% RH, the remaining water contents are 92%, 89% and 82% at ~92% RH, corresponding to OIR of 2:1, 1:1 and 1:2 mixed system, respectively.

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Introduction

Atmospheric aerosols influence global climate directly or indirectly and are also one of the major factors deteriorating air quality (Ravishankara et al., 2015; Moise et al., 2015). At a certain relative humidity (RH), the interactions between water vapor and aerosol particles can leads to liquid water absorption in particles (Krieger et al., 2012). The water absorption capacity of aerosol particles is highly influenced by their chemical composition, mixed state and RH (Ma et al., 2013).

The particles containing liquid water content may affect solar radiation, human health, atmospheric visibility, wet and dry deposition, aerosol acidity and heterogeneous chemical reactions (Akimoto, 2003; Farmer et al., 2015; Hallquist et al., 2009).

The carbonate can exert a strong influence on the transport of contaminant metals. In solution, carbonate can react with metals to form insoluble minerals or soluble complexes, depending on the metal involved and the pH. Gillette et al. (1992) reported emissions of alkaline elements.
(Ca, Mg, K, and Na) from soils in the southwestern United States, primarily in the form of carbonates. Sturges et al. (1989) collected aerosol samples in suburban Toronto, Canada, between January and July 1986, and observed carbonate concentrations to be 1–2 μg/m³ (about 6% of the total mass), with summer concentrations slightly higher due to the greater degree of construction activity Clarke and Karani (1992) found that in the atmosphere of the city of Leeds, U.K., carbonate comprised 2%–3% of the coarse particulate mass. Based on detected carbonate contention, they believed that the fine particles contained apparently volatile carbonate for which the most likely source is the surface of soot particles.

Although there are still no accurate contention of sodium carbonate reported to our knowledge, the gas–aerosol partition equilibrium of carbonate has been calculated by Meng et al. (1995). They reported that the species considered include CO₂(g), CO₂(aq), HCO₃⁻, CO₃²⁻, Na₂CO₃(s), NaHCO₃(s), and so on. On the surface of either sodium solution or/and sodium aerosol, CO₂ absorption and uptake take place and then heterogeneous hydrolysis leads to CO₃²⁻ ions in the presence of water, which combine with Na⁺ to form Na₂CO₃ (Hua et al., 2011; McGillis and Wanninkhof, 2006). In laboratory and field study, the hygroscopicity of many sodium salt aerosols containing Na₂SO₄, NaCl and NaNO₃ have been measuring its deliquescence relative humidity (DRH) and efflorescence relative humidity (ERH) (Darr et al., 2014; Feng et al., 2014; Pope et al., 2010; Lu et al., 2008). Nonetheless, hygroscopicity of Na₂CO₃ aerosol has no report to the best of our knowledge. Considering the increasing concentration of CO₂ in the atmosphere (~385 ppm, IPCC 2007) and abundant marine sodium ions, the hygroscopic behavior of carbonate from reaction of CO₂ with water may be important.

Atmospheric amino acids, coming from plant debris, pollen, fungi and bacteria spores in continental particles (Matsumoto and Uematsu, 2005) and sea spray particles owing to Bubble bursting and jet drop production (Seinfeld and Pandis, 2006; Bertram et al., 2018), and have been confirmed as effective cloud condensation nuclei (CCN) materials in laboratory experiments (Kristensson et al., 2010). Usually, the three types of amino acids are classified in aerosols, and they are dissolved combined amino acids, i.e. proteins and peptides, dissolved free amino acids and particulate amino acids (Kuznetsova et al., 2005; Milne and Zika, 1993; Mopper and Zika, 1987). The source contributions of these amino acids have been well characterized (Wedyan and Preston, 2008; Zhang and Anastasio, 2003; Mader et al., 2004), while the hygroscopicity work on amino acid aerosols is not exhaustive (Na et al., 1995; Wang et al., 2018a). For example, Chan et al. (2005) examined the hygroscopic properties of several amino acids using an electrodynamic balance (EDB) and compared their work to universal quasi-chemical functional group activity coefficients (UNIFAC) predictions. In 2017, Reid and co-workers (Marsh et al., 2017) also used a variation of the EDB technique to measure the hygroscopicity of several amino acids in terms of the Köhler parameter, κ, based upon κ-Köhler theory. Their results were distinguished from those of Chan and co-workers. In the work referenced above, amino acid measured is α type, often used as the building blocks of proteins. In fact, α-aminoacids, participate directly, as information carrier molecules, in the neurotransmission processes occurring in the mammalian nervous system, have deserved much less attention.

Atmospheric aerosols are mostly complexes, composed of inorganic and organic species, including inorganic salts, sulfates, nitrates, metals and organic compounds, such as acids, alcohols, amino acids and sugars (Mikhailov et al., 2004; Baltensperger, 2016; Seinfeld and Pankow, 2003; Zhang et al., 2015). Pure inorganics and organics have been studied extensively, and their hygroscopic properties, particularly its deliquescence relative humidity (DRH) and efflorescence relative humidity (ERH), are well-known. Recently, increased attention has been devoted to examining the deliquescence and efflorescence of inorganic salts in internally mixed organic/inorganic aerosols (Wang et al., 2018b; Wang et al., 2017). However, the study on amino acid-inorganics is absent. In 2018, Darr et al. (Darr et al., 2018) studied the hygroscopicity in sub-micron sodium chloride-amino acid aerosols and summarized the effect of several amino acids on hygroscopicity of NaCl in internally mixed NaCl-amino acid aerosols generated from an

![Fig. 1 – FTIR spectra of Na₂CO₃ aerosols on (a) dehydration and (b) hydration. The bottom blue spectrum in (a) comes from Na₂CO₃ powder, the red line in (b) is the IR spectrum of Na₂CO₃·H₂O crystal.](image-url)
The mixture of Na$_2$CO$_3$ and alanine should cause our concern though there are no available field-measured data reported to date. In this paper, the focus is the hygroscopic properties of Na$_2$CO$_3$, $\beta$-alanine and internally mixed $\beta$-alanine/Na$_2$CO$_3$ particles at different mole ratios. The experiment has been performed with ATR-FTIR spectroscopy. Upon our experiments, we analyzed the crystallization and deliquescence of $\beta$-alanine and Na$_2$CO$_3$, and water content with the RH in mixing system. As far as we know, it is the first time to report the Na$_2$CO$_3$ and $\beta$-alanine.

### 1. Materials and methods

#### 1.1. Aerosols preparation

We prepared 0.5 mol/L Na$_2$CO$_3$ and $\beta$-alanine aqueous solution by dissolving Na$_2$CO$_3$ (99.0% purity, Beijing Chemical Regents Company) and $\beta$-alanine (99.5% purity, Alfa Aesar) into triply deionized water (produced by Beijing Institute of Technology), respectively. The mixed alanine/Na$_2$CO$_3$ aqueous solutions were prepared by adding designed amounts of $\beta$-alanine into 50 mL Na$_2$CO$_3$ aqueous. All chemicals were used directly without further treatment. The aerosol particles were prepared by a nebulizer and the sizes of particles are 2–8 $\mu$m. When the particles are deposited on a ZnSe crystal substrate with a pump, the RH of chamber is kept up to higher than 85% for ensuring mixed aerosol as droplets.

#### 1.2. Experimental setup

ATR-FTIR technology is not sketched out herein because it has been described in detail in our previous works (Zhang et al., 2014). FTIR spectrometer comes from Nicolet Co. (model Magna-IR560) with a liquid-nitrogen-cooled MCT detector. The sample chamber comprised a baseline horizontal ATR accessory (Spectra-Tech Inc. USA) with a ZnSe substrate. The RH in the chamber, adjusted by mixing streams of dry and humidified N$_2$ gas with the total flow rates of 400 mL/min, is recorded by a RH & temperature detector (CENTER 313, ±2.5% RH, ±0.7°C). On measurement, the aerosols were first performed through the dehydration process, followed by a humidification process to finish a RH cycle. The spectra were collected with a resolution of 4 cm$^{-1}$ between 4000 and 650 cm$^{-1}$ with 32 scans. To ensure the certainty of spectral

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**Table 1 – Band assignment of IR bands for $\beta$-alanine and Na$_2$CO$_3$.**

<table>
<thead>
<tr>
<th>$\beta$-Alanine</th>
<th>Na$_2$CO$_3$</th>
<th>Assignments</th>
</tr>
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<tbody>
<tr>
<td>Aqueous Solid</td>
<td>Aqueous Solid</td>
<td></td>
</tr>
<tr>
<td>2928 $\nu_{as}$(CH$_2$)</td>
<td>1573 $\nu_{as}$(CO$_2$)</td>
<td></td>
</tr>
<tr>
<td>2880 $\nu_{as}$(CH$_2$)</td>
<td>1573 $\nu_{as}$(CO$_2$), $\delta$(NH$_3$)</td>
<td></td>
</tr>
<tr>
<td>1634 $\delta$(NH$_2$)</td>
<td>1508 $\nu_{as}$(CO$_2$)</td>
<td></td>
</tr>
<tr>
<td>1573 $\nu_{as}$(CO$_2$), $\delta$(NH$_3$)</td>
<td>1424 $\nu_{as}$(CO$_2$)</td>
<td></td>
</tr>
<tr>
<td>1408 1414, 1403 $\omega$(CH$_3$)</td>
<td>1380 $\nu$(CH$_3$)</td>
<td></td>
</tr>
<tr>
<td>1397 1387 $\nu$(CH$_3$)</td>
<td>1380 $\nu$(CO$_3$)</td>
<td></td>
</tr>
<tr>
<td>1334 1334 $\nu$(CH$_3$)</td>
<td>1262 $\nu$(CH$_2$)</td>
<td></td>
</tr>
<tr>
<td>1294 1300 $\tau$(CH$_2$), $\omega$(CH$_3$)</td>
<td>1156 $\nu$(C-O), $\omega$(NH$_3$)</td>
<td></td>
</tr>
<tr>
<td>1108 1061 $\omega$(NH$_3$)</td>
<td>1108 1061 $\omega$(NH$_3$)</td>
<td></td>
</tr>
<tr>
<td>1053 991 $\nu$(C-N)</td>
<td>973 991 $\nu$(C-N)</td>
<td></td>
</tr>
<tr>
<td>973 991 $\nu$(CH$_3$)</td>
<td>943 927 $\nu$(CH$_2$) + $\tau$(NH$_3$)</td>
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<tr>
<td>943 927 $\nu$(CH$_3$) + $\tau$(NH$_3$)</td>
<td>943 927 $\nu$(CH$_2$) + $\tau$(NH$_3$)</td>
<td></td>
</tr>
<tr>
<td>885 887 $\nu$(C-CD$_2$)</td>
<td>885 887 $\nu$(C-CD$_2$)</td>
<td></td>
</tr>
<tr>
<td>839 844 $\delta$(CO$_3$) l.p.</td>
<td>839 844 $\delta$(CO$_3$) l.p.</td>
<td></td>
</tr>
</tbody>
</table>

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**Fig. 2 – FTIR spectra of $\beta$-alanine aerosols on (a) dehydration and (b) hydration. In (a), the yellow curve is the spectra of $\beta$-alanine solid powder.**
signals, measurement of every sample with is repeated more than three times.

1.3. Data processing

In order to eliminate features in the spectra due to gas phase water vapor, the aerosol-free spectra were subtracted from the aerosol spectra. In the resulting differential spectrum, the liquid water peak spanning 3324–3500 cm⁻¹ was integrated in order to monitor the water content of aerosol particles. For internally mixed alanine/Na₂CO₃, the band at 877 cm⁻¹ was integrated to characterize the solid Na₂CO₃ and the integrated wavenumber range is 892–864 cm⁻¹, and the band at 2950 cm⁻¹ represents the solid alanine and the integrated range is 2900–2975 cm⁻¹. The integration was performed by Omnic software without baseline-corrected. The uncertainty associated with an integrated data of each experimental process is ~5% through three time of measurements.

2. Results and discussion

2.1. FTIR spectra of aerosol particles with a dehydration–hydration cycle

The chemical compositions are monitored by ATR-FTIR spectra. IR spectra of pure Na₂CO₃ aerosols with RH can be found in Fig. 1 and the band assignments are assigned in Table 1. (Kiefer et al., 2018; Morisset et al., 2018) The broad bands at ~3373 and 1648 cm⁻¹ are attributed to the stretching vibration (ν-OH) and bending mode (δ-OH) of OH group in water molecules, which can characterize the water content in aerosols. During the dehydration process (Fig. 1a), the ν-OH and δ-OH bands decrease, implying lower water content. The broad band at 1380 cm⁻¹, assigned to the asymmetric stretch mode of carbonate (ν₁-αCO₃), becomes stronger. It is well known that the band intensity is dependent upon the concentration. When the ambient RH decreases, the water content in aerosol particles become lower owing to keep equilibrium to ambient vapor, in turn, the concentration of Na₂CO₃ increases. When the RH drops to 59.8%, two new sharp peaks at 1422 and 877 cm⁻¹ suggest the solid Na₂CO₃ formation supported by the IR spectrum of solid powder Na₂CO₃ (show in the bottom blue curve of Fig. 1a). While the band at 1380 cm⁻¹ degenerates into a visible broad shoulder, together with the sudden decrease in water content. As the RH continues to decrease, the feature bands from carbonate become stronger, indicating more solid Na₂CO₃. At 4.6% RH, the bands at 1380 and 3373 cm⁻¹ almost vanish, meaning complete crystal.

During hydration process (shown in Fig. 1b), water content increases slowly with the RH and features of Na₂CO₃ keep constant at 1422 and 877 cm⁻¹. When the RH goes up to 72.0%, the band at 1422 cm⁻¹ splits into two peaks at 1436 and 1407 cm⁻¹ and the band at 877 cm⁻¹ shifts to 856 cm⁻¹, which compares well with the absorbance of the carbonate with Na₂CO₃·H₂O solid powder (Kiefer et al., 2018) (red line in Fig. 1b), indicating the Na₂CO₃·H₂O formation. The presence of some water molecules in the crystal lattice seems to enhance the IR activity, which goes along with a change in the dipole moment of the carbonate groups. Again, the presence of water molecules leads to additional bands at 2969 and 1730 cm⁻¹, which are due to OH stretching and bending vibrations. At 89% RH, the bands at 1436 and 1407 cm⁻¹ merge into a broad band at 1380 cm⁻¹, showing solution state of Na₂CO₃ particles. So, the change routes of Na₂CO₃ physical phase between solution and solid on hydration and dehydration were not reverse completely.

β-Alanine is an important amino acid, whose hygroscopicity is still unknown. Fig. 2 describes the IR spectra dependent upon the RH and the assignment is summed in Table 1 (Garcia et al., 2008; Rosadoa et al., 1997). At high RH of 92%, the broad bands at 1570, 1406, 1385 cm⁻¹ are strong, as well as some weak absorptions at 1335, 1294, 1109 and 838 cm⁻¹. The broad band at ~3373 cm⁻¹ is owing to liquid water in droplets. As the RH decreases, the water peak becomes lower accompanying a broad absorption in the range from 3310 to 2600 cm⁻¹, which should be caused by overlapped bands from –NH₂, –CH₂ and –COOH groups. Above 37% RH, no distinct spectral change of alanine is found. Upon 37.7% RH, the band at ~1570 cm⁻¹ becomes narrower and takes a slight shift, two sharp and strong peaks at 1631 and 1506 cm⁻¹ arise. In high wavenumber region, four small peaks from 3100 to 2600 cm⁻¹ emerge. Again the characteristic vibrations of –COOH and –NH₂ become more structured. More concretely, the sharp triplet peak at 1414, 1404 and 1387 cm⁻¹ appears and other peaks below 1350 cm⁻¹ become sharper and stronger. Comparison the IR spectra of particles at 37.7% RH and that of β-alanine powder (yellow line in bottom of Fig. 2a) finds the same band feature. So the crystalline β-alanine particles can be confirmed. With the RH continues to reduce gradually, water content becomes lower with little changeable other peaks.

On humidifying (Fig. 2b), the feature bands exhibit no perceptible change besides features becoming lower. Up to 91.8% RH, the feature bands suddenly evolve to that of β-alanine droplets, similar to absorbance of initially atomized droplets, showing aqueous state.

In order to detect the effect of mixing Na₂CO₃ with β-alanine on IR spectra, Fig. 3a compares the spectra from pure β-alanine, pure Na₂CO₃ and mixed β-alanine/Na₂CO₃ droplets. Obviously, the addition of Na₂CO₃ weakens the peaks at 1335, 1330 and 1106 cm⁻¹ due to interaction between CO₃²⁻ and β-alanine. Another IR band at ~1385 cm⁻¹ becomes stronger upon increasing Na₂CO₃ content. By contrast, the feature bands from Na₂CO₃ are almost completely hidden or overlapped in aqueous state comparing to spectrum of pure Na₂CO₃. Fig. 3b-d summarizes the FTIR spectra of mixed aerosols with different OIRs on dehydration. For particles with 2:1 OIR (Fig. 3b), the water envelopes at ~3373 and 1640 cm⁻¹ damped straightly with the RH. When the RH falls to ~62% RH, the faint bands at 2950 cm⁻¹ peep out. From enlarged 10 fold spectrum at 3.6% RH (inset of Fig. 3), the band at 877 cm⁻¹ is visible, ensuring solid Na₂CO₃. With the continuous RH decrease, these changes become apparent. For 1:1 alanine/Na₂CO₃ aerosols seen in Fig. 3c, an analogous spectral evolution occurs on dehydration. Like above 2:1 situation, the absorptions at 2950 and 877 cm⁻¹ are more obvious with
the decrease in RH. As for particles with the OIR of 1:2 (Fig. 3d), the landmark band of solid Na₂CO₃ lies at 1421 cm⁻¹ besides 877 cm⁻¹ owing to enriched Na₂CO₃ content as lower RH. Fig. 3e presents the spectra from pure β-alanine, pure Na₂CO₃ and mixed β-alanine/Na₂CO₃ solids. By contrast, the bands at 2950 cm⁻¹ and that at 877 cm⁻¹ are decided as the feature of solid β-alanine and solid Na₂CO₃. The hydration process behaves converse spectral trends for studied mixed system (seen in Fig. 4).

Fig. 3e compares the spectra of pure component and mixed particles in solid state, which decide the signs of solid β-alanine and Na₂CO₃ corresponding to the bands at 2950 and at 877 cm⁻¹, respectively. Therefore, their integrated areas are utilized to evaluate the phase transition of components, respectively, in 1:1 and 1:2 mixed β-alanine/Na₂CO₃ aerosols. In Fig. 5a, the band area of 877 cm⁻¹ keeps almost unchanged for 2:1 β-alanine/Na₂CO₃ aerosols, as a result of too weak band at 877 cm⁻¹ from Na₂CO₃ solid formation. For 1:1 mixed particles, the sudden increase is from 51.8 to 42.3% RH. Outside of the range, the change is gradual. When the OIR is 1:2, the aqueous–solid transition takes place in the range of 57.1%–42.3% RH. From the band area of 2950 cm⁻¹ peaks, the phase behavior of β-alanine can be acquired. From Fig. 5b, β-alanine begins to form solid 

![FTIR spectra comparison](image)

Fig. 3 – (a) FTIR spectral comparison between pure β-alanine, alanine/Na₂CO₃ (OIR = 2:1, 1:1 and 1:2) and pure Na₂CO₃ droplets, (b) spectra of β-alanine/Na₂CO₃ aerosols 2:1, (c) 1:1 and (d) 1:2 on dehydration process, (e) IR spectra of pure β-alanine, pure Na₂CO₃ and β-alanine/Na₂CO₃ solid particles (OIR = 2:1, 1:1 and 1:2).
from 62.7% RH for 2:1 aerosols and from 58.8% RH for 1:1 and 1:2 mixtures. Till to least RH, solid always increases reflected by increasing band area on dehydration. On hydration, Na$_2$CO$_3$ deliquesces in the RH range from 44.7% to 75.2% and from 44.7% to 69.0% RH for 1:2 and 1:1 $\beta$-alanine/Na$_2$CO$_3$ aerosols, respectively (shown in Fig. 5c). In the case of $\beta$-alanine, it takes transition from solid to solution from 68.9% RH for both 1:1 and 1:2 particles, and from 74.8% RH for 2:1 mixing system (Found in Fig. 5d).

2.2. Water uptake of aerosol particles

The changeable liquid water content is often used to describe the hygroscopicity along with the RH increases or decreases, and abrupt water content change corresponds to the phase transition. But, the more valid evidence of phase state should combine the envelopes of physical state. Fig. 6 gives the water content curves of Na$_2$CO$_3$ and $\beta$-alanine as a function of RH during dehumidifying-humidifying cycle in different systems. As seen from Fig. 6a, the rapid water decrease takes place from 62.9% to 51.9% RH on dehydration and from 72.0% to 80.1% RH on hydration for pure Na$_2$CO$_3$ particles. With a view to spectral change in Fig. 1, it can be concluded that efflorescence RH (ERH) is 62.9%–51.9% RH for pure Na$_2$CO$_3$ particles. However, the Na$_2$CO$_3$·H$_2$O formation should be from 72.0% to 80.1% RH. From 84.5% RH, the aqueous Na$_2$CO$_3$ solution formed. For $\beta$-alanine droplets in Fig. 6b, the sudden water loss and absorption occur in the range of 42.4%–33.2% RH and at 88.2% RH, showing the ERH and DRH, respectively.

Having determined the hygroscopic behavior of pure $\beta$-alanine, Na$_2$CO$_3$, we next sought to determine the mutual effect of Na$_2$CO$_3$ and $\beta$-alanine on DRH and ERH on hydration and dehydration in $\beta$-alanine/Na$_2$CO$_3$ mixtures. Fig. 7a–c shows the resulting water uptake and release plots for aerosols generated from the 2:1, 1:1 and 1:2 precursor solutions of $\beta$-alanine/Na$_2$CO$_3$, respectively. For OIR of 2:1, particles exhibit a continuous absorption or release of water (seen in Fig. 7a) without sudden change for two RH cycles. During the first dehydration–hydration cycle, water content on dehydration is lower than that on hydration above 70% RH range. At 92% RH, water content decreases 18% compared to origin droplets. For aerosols generated from an equimolar solution of $\beta$-alanine and Na$_2$CO$_3$, water release becomes rapidly at ~52.0% RH on dehydration found in Fig. 7b, which is identical as only the onset of Na$_2$CO$_3$ crystallization (51.8% RH). In the hydration plot, water uptake increases in an approximately linear fashion. In the second down-up RH cycle, water content changes both linearly. When the Na$_2$CO$_3$ is enriched shown in Fig. 7c (OIR = 1:2), there appears the sudden water-loss regions from 62.8% to 43.2% RH obviously on first dehydration and from 62.8% to 52.2% RH on second dehydration. And water uptakes change at 76.1% RH on hydration. Above paragraph has shown that 62.8% RH

![Fig. 4 – FTIR spectra of alanine/Na$_2$CO$_3$ aerosols with the different $\beta$-alanine:Na$_2$CO$_3$ mole ratios (a) 2:1 (b) 1:1 and (c) 1:2 on hydration process.](image-url)
is the onset of β-alanine crystal and 42.3% is the end of solid Na₂CO₃. Hence, the abrupt water loss should be caused by solid β-alanine and Na₂CO₃ formation. In the hydration curve, water uptake becomes slower at ~76% RH, which is the end of Na₂CO₃ (in Fig. 5c). During the following second dehydration, there is a water loss inflection at 62.8% on dehydration and at ~76% RH on hydration. Therefore, based on these analysis, water uptake and loss trends reflect more obvious for phase transition of Na₂CO₃ than β-alanine and the more plots changes in first RH cycle.

Darr et al. (2018) reported the effect of hydropathy scale of several amino acid on hygroscopicity. They found that the amino acids including the hydrophobic side chain, for example, DL-alanine and DL-valine, have no significant deviation from the hydration and dehydration of pure NaCl. While that containing the hydrophilic side chain, for example, glycine, significantly alter the hygroscopic properties of NaCl hydration and dehydration of pure NaCl. In Fig. 6, there is the characteristic deliquescent and efflorescent phenomena are observed with the deliquescence occurring at 88.2% and efflorescence occurring between 42.4% and 33.2% RH for pure β-alanine. Analysis on the chemical structure of β-alanine, the amine is located at the end of chain, which is like glycine, while, it also has the same
molecular formula to DL-alanine. So, the effect of β-alanine has less effect on hygroscopicity of Na₂CO₃ compared to that of glycine to NaCl. Yet, the effect is stronger than DL-alanine.

Fig. 7d compares the water loss at 92% after the first down-up RH cycle, the water contents are 0.82, 0.89 and 0.92 at 92.4% RH at OIR of 2:1, 1:1 and 1:2. Obviously, more Na₂CO₃ leads to less water-loss. The previous study believed that chemical evolution in particles and incomplete deliquescence (Yang et al., 2019; Wang et al., 2017) often lead to water lost. Nevertheless, the present IR spectra display no changeable compounds and Fig. 5c, d shows complete deliquescence. So the exact cause of water loss needs to be investigated further by other technologies or methods.

3. Conclusions

In this study, the phase transition and hygroscopicity of pure sodium carbonate aerosol particles are measured initially. It reveals the formation of sodium carbonate monohydrate at 72% RH or so on hydration, and then transforms solution at 84.5% RH, which is first reported to our knowledge. Pure β-alanine effloresces at 42.4%–33.2% RH and deliquesces at ~88.2% RH. When β-alanine is mixed with sodium carbonate, crystallization of sodium carbonate is delayed from 62.9%–51.9% range to 57.1%–42.3% for 1:2 OIR (or 51.8%–42.3% for 1:1 OIR) and efflorescence onset of β-alanine is promoted from 42.4% RH to 62.7% for 2:1 OIR (or 59.4% RH for both 1:1 and 1:2 OIR). After a dehydration-hydration cycle, water content in particles decreases and decrement is 0.18, 0.11 and 0.08 for OIR of 2:1, 1:1 and 1:2, respectively. The present results somewhat fill in the gap of carbonate and enrich the studies on β-alanine.

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