

**Atmospherically
relevant
water-soluble
carboxylic salts**

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Hygroscopic behavior of atmospherically relevant water-soluble carboxylic salts and their influence on the water uptake of ammonium sulfate

Z. J. Wu, A. Nowak, L. Poulain, H. Herrmann, and A. Wiedensohler

Leibniz Institute for Tropospheric Research, Permoserstr. 15, 04318 Leipzig, Germany

Received: 3 February 2011 – Accepted: 28 February 2011 – Published: 7 March 2011

Correspondence to: Z. J. Wu (wuzhijun@tropos.de)

Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

The hygroscopic behavior of atmospherically relevant water-soluble carboxylic salts and their effects on ammonium sulfate was investigated using a hygroscopicity tandem differential mobility analyzer (H-TDMA). No hygroscopic growth is observed for sodium oxalate, while ammonium oxalate shows slight growth (growth factor = 1.05 at 90%). The growth factors at 90% RH for sodium acetate, sodium malonate, sodium succinate, sodium tartrate, ammonium tartrate, sodium pyruvate, sodium maleate, and humic acid sodium salt are 1.79, 1.78, 1.69, 1.54, 1.29, 1.70, 1.78, and 1.19, respectively. The mixtures of organic salts with ammonium sulfate, which are prepared simulating the atmospheric aerosols, are determined. A clear shift in DRH of mixture to lower RH is observed with increasing organic mass fraction. Above RH = 80%, the humidograms of the different mixtures are quite close to that of pure ammonium sulfate. Köhler theory is used to predict the effective hygroscopicity parameter, κ , for mixtures at 90% RH. The results show that Köhler theory underestimated κ for mixtures without considering the water solubility of ammonium oxalate. However, if the water solubility of ammonium oxalate is taken into account, the results show a much better agreement with those derived from H-TDMA measurements.

1 Introduction

In the atmosphere, aerosol hygroscopicity plays an important role in cloud formation, visibility degradation, and atmospheric chemistry (Pandis et al., 1995; Sloane and Wolff, 1985; McFiggans et al., 2006). During the past 20 years, the importance of hygroscopic properties of atmospherically relevant inorganic salts was recognized. However, the influence of water uptake of the organic aerosol fraction, which contribute 20–90% of atmospheric fine aerosol mass, still remains unclear (Kanakidou et al., 2005; Zhang et al., 2007; Hallquist et al., 2009). A substantial portion of organic aerosols is water soluble organic matter (WSOM) (Saxena and Hildemann, 1996), including low

ACPD

11, 7693–7714, 2011

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molecular weight carboxylic acids (e.g., Kawamura and Gagosian, 1987; Legrand et al., 2007; Kawamura et al., 1996) and macromolecular humic-like substances (HULIS) (Graber and Rudich, 2006), which can considerably influence the hygroscopic behavior of the inorganic aerosol (Decesari et al., 2003; Saxena and Hildemann, 1996; Choi and Chan, 2002). These organic acids may neutralize gas-phase ammonia and/or associate with cations such as sodium and potassium in the particle phase. Thereby organic salts are formed, which show rather different thermodynamic properties from their acids (Peng and Chan, 2001). Typically, sodium salts of organic acids can be found in marine aerosol particles (Kerminen et al., 1998). In other atmospheric environments, such as in the Amazon Basin, the aerosol ion balance calculation shows that in the presence of excess inorganic base, organic acids can act to neutralize particles (Mircea et al., 2005; Trebs et al., 2005; Metzger et al., 2006) to form organic salts. Recently, the formation of organic salts such as aminium salts was proposed to be a pathway for contribution of low molecular weight organic compounds to atmospheric nanoparticle growth (Barsanti et al., 2009; Smith et al., 2010). Laboratory studies of the reactive uptake of ammonia onto slightly soluble organic acid particles found that this process can significantly increase the CCN activity and hygroscopic growth of these particles (Dinar et al., 2008; Mircea et al., 2005). These evidences indicate that organic salts instead of their acids might play important roles under certain circumstances in the atmosphere.

Previous laboratory studies, investigating the hygroscopicity of organic substances, mainly focused on organic acids using a Hygroscopicity Tandem Differential Mobility Analyzer (H-TDMA) or an electrodynamic balance (EDB) (Kanakidou et al., 2005). Conversely, the investigations on their salts are very sparse (Kanakidou et al., 2005). An investigation of the water cycles of water-soluble organic salts of atmospheric interests was performed by Peng and Chan (2001) using an EDB. Their results showed that sodium salts of formate, acetate, malonate, succinate, maleate, and pyruvate have a growth factor of 1.76–2.18 at a relative humidity of 90%. The EDB method, however, is typically used for particles larger than a few micrometres in diameter and not

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suitable for studies of hygroscopic growth of fine atmospheric aerosol particles (Swietlicki et al., 2008). The hygroscopic growth of a sodium salt of humic acid (growth factor (GF) = 1.08 at 90% RH) has been determined using H-TDMA by several studies (e.g. Gysel et al., 2004), and showing that it is slightly more hygroscopic than humic acid (GF = 1.06 at 90% RH). The effect of organic compounds on the hygroscopicity of atmospherically relevant inorganic salts were widely investigated in previous studies (e.g. Cruz and Pandis, 2000; Zardini et al., 2008; Svenningsson et al., 2006; Choi and Chan, 2002). Again, they mainly focused on the roles of organic acids.

In this study, we determine the hygroscopic growth of atmospherically relevant organic salts using a H-TDMA. Furthermore, their mixtures with ammonium sulfate, which is one of the most abundant inorganic constituents found in the atmosphere (Seinfeld and Pandis, 1998), are investigated to determine the influence of organic salts on the hygroscopic behaviors of ammonium sulfate. In addition, we use Köhler theory (Peters and Kreidenweis, 2007) to calculate the effective hygroscopicity parameter κ of mixtures based on the hygroscopicity of the individual compounds.

2 Experiments

2.1 Instrumentation

The hygroscopic growth of particles is investigated using a H-TDMA. The H-TDMA used in this study was employed in various field studies and is described in detail by Massling et al. (2003, 2007). Only a brief description is given here. The H-TDMA consists of three main parts: (1) A Differential Mobility Analyzer (DMA1) that selects quasi-monodisperse particles, and a Condensation Particle Counter (CPC1) that measures the particle number concentration leaving the DMA1 at the selected particle size; (2) An aerosol humidifier conditioning the particles selected by DMA1 to a defined relative humidity; (3) The second DMA (DMA2) coupled with another condensation particle counter (CPC2) to measure the number size distributions of the humidified aerosol.

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To ensure the stability of the RHs, the proportional–integral–derivative (PID) controlling method is utilized to regulate the RHs for both aerosol humidifier and sheath air of DMA2. In addition, DMA2 and aerosol humidifier are kept inside of a temperature-controlled box to avoid the temperature fluctuation higher than 0.3 K. Capacitive RH sensors (Model HMP237, VAISALA Inc.) used to monitor the conditions in the H-TDMA are regularly calibrated against a dew point hygrometer (the same dew point hygrometer used to measure the RH in DMA2) during the measurements. The experiments were conducted in the lab, in which the room temperature is air-conditioned to be within 20 ± 1 °C.

The hygroscopic growth factor (GF) is defined as the ratio of the particle mobility diameter, $D(\text{RH})$, at a given RH to the dry diameter, D_d , 100 nm in this study:

$$\text{GF}(\text{RH}) = \frac{D(\text{RH})}{D_d}. \quad (1)$$

The inversion of the H-TDMA data is based on TDMA_{inv} method developed by Gysel et al. (2009). Dry scans (under RH < 5%) are used to calibrate any size shift between DMA1 and DMA2 and define the width of the HTDMA's transfer function (Gysel et al., 2009) for each compound being measured.

2.2 Aerosol generation

A nebulizer was used to generate particles from a solution of selected organic compounds as listed in the first column of table 1, diluted in ultra-pure water (18.2 MΩcm at 25 °C; Milli-Q Academic, Millipore, USA). Humic acid sodium salts cannot be completely dissolved in the water. In order to remove the non-dissolved material, the solution was filtered through a paper filter with a 2 μm pore size. The generated particles were dried by passing through a diffusion drier filled with silica gel, and then mixed with pure dry air in a glass mixing chamber. The RH of the sampling air flow was kept below 5% and monitored by a RH sensor mounted in the inlet of H-TDMA.

Hygroscopic growth of an ammonium sulfate aerosol was measured first to compare with the predicted growth using the parameterizations given by Tang and Munkelwitz (1994) and thus to validate the accuracy and performance of the H-TDMA. Afterwards, the hygroscopic growth factors of the organic salts as listed in the first column of table 1 were determined. All salts being studied are the products of Sigma-Aldrich Company (www.sigmaaldrich.com). The purity of reagent was greater than or equal to 99%.

2.3 Measurement uncertainty

The measurement uncertainty of H-TDMA significantly depends mainly on the accuracy in RH within the system but also on a possible size shift between the two DMAs (Massling et al., 2007). The particle size shift between DMA1 and DMA2 for the entire data set was calibrated using the dry scans (non-humidified particle sizing). The estimated uncertainty in measurements between 30% and 90% RH was $\pm 1\%$ RH. Correspondingly, this uncertainty results in a relative uncertainty of around 2.5% for growth factors of ammonium sulfate particles measured at 90% RH (Massling et al., 2003).

3 Results and discussion

3.1 Pure organic salts

The GFs of organic salts as a function of RH are presented in Fig. 1. They are parameterized using a polynomial fit, and the fitting parameters are summarized in Table 1. According to these polynomial fitting parameters, the growth factors at 90% are calculated and also shown in the Table 1. The hygroscopicity of individual carboxylic salt will be discussed in the following.

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3.1.1 Sodium acetate

As shown in Fig. 1a, the deliquescence relative humidity (DRH) of sodium acetate is around 40% (39–42%), which is slightly lower than that (43.5–45.2%) observed by Peng and Chan (2001) using an EDB. This may cause by different diameters of the particles being measured in Peng and Chan and this study (see Hämeri et al., 2000).

3.1.2 Sodium oxalate and ammonium oxalate

Sodium oxalate has a low solubility (3.41 g/100 g water at 20 °C). No hygroscopic growth was observed below 90% RH, as shown in Fig. 1b. This is consistent with the previous results from the EDB (Peng and Chan, 2001) and H-TDMA (Mensah et al., 2009) measurements. Mensah et al. (2009) observed that sodium oxalate particles start to take up water above 92.2% RH.

Similar to sodium oxalate, the solubility of ammonium oxalate (4.45 g/100 g water at 20 °C) is very low. Below 30% RH, no growth is observed. Above this RH, the GF is constant and around 1.05. This hygroscopic behavior is in agreement with that observed using H-TDMA by Mensah et al. (2009) below 90%. Their results show that DRH of ammonium oxalate is 93.3%.

3.1.3 Sodium malonate

As shown in Fig. 1c, sodium malonate continues to grow with increasing RH, and no deliquescence point is observed, similar to the behavior reported by Peng and Chan (2001).

3.1.4 Sodium succinate

Similar to sodium malonate, no deliquescence point is observed for sodium succinate, as shown in Fig. 1d. This is different from the observation using an EDB by Peng and Chan (2001), whose result shows the DRH is 63.5–66%. The reason is unclear.

3.1.5 Sodium tartrate and ammonium tartrate

The hygroscopic growths for sodium tartrate and ammonium tartrate are presented in Fig. 1e. Both salts continue to grow above 40% RH. The sodium salt is more hygroscopic than the ammonium salt.

3.1.6 Sodium pyruvate

The DRH of sodium pyruvate is around 82%, which is within the DRH (71.6–83.9%) observed by Peng and Chan (2001). In Peng and Chan's study, they observed that sodium pyruvate shows a gradual deliquescence process and kept absorbing water at RH = 79% even after 11 h. They ascribed it to the internal mass transfer limitation of the particle during growth. However, this was not observed using H-TDMA in our study.

3.1.7 Sodium maleate

As shown in Fig. 1g, sodium maleate particles start to grow at RH above 20%. Afterwards, particles continuously take up water with the increasing RH.

3.1.8 humic acid sodium salts

The hygroscopic growth of humic acid sodium salts has been investigated by several previous laboratory studies (Badger et al., 2006; Gysel et al., 2004; Hatch et al., 2009). Gysel et al. (2004) observed that humic acid sodium salts deliquesces at RH between 60–75%. Whereas, no deliquescence behavior is found by Badger et al. (2006)'s study. Similarly, our observation, as displayed in Fig. 1h, shows that the humic acid sodium salts particles continuously grow with increasing RH.

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3.2 Mixtures of organic salts with $(\text{NH}_4)_2\text{SO}_4$

Three mixtures are investigated to determine the influences of organic salts on the hygroscopicity of ammonium sulfate. These mixtures are prepared according to the chemical composition of the atmospheric particles reported in literature assuming carboxylic salts instead of carboxylic acids in the atmospheric aerosols. Oxalic acid is assumed to neutralize by ammonia, i.e, forming ammonium oxalate, and others are assumed as sodium salts. Their chemical compositions are given in Table 2. Mix_urb, Mix_mar, and Mix_bio represent urban aerosols in Hong Kong (Yao et al., 2004), marine aerosols in Mace Head (Kleefeld et al., 2002), and biomass burning aerosols in Brazil (Kundu et al., 2010a, b), respectively.

3.2.1 Effect of organic salts on the deliquescence

The humidograms of mixtures and pure ammonium sulfate are shown in Fig. 2. There is a clear shift in DRH to lower RH with increasing organic mass fraction, indicating that these organic salts have significant effects on the deliquescence of ammonium sulfate. With increasing organic mass fraction, a smoothing of the deliquescence behavior is observed. This phenomenon was also observed for mixtures of ammonium sulfate and individual dicarboxylic acids such as citric acid, succinic acid, and malonic acid by previous studies (e.g. Zardini et al., 2008; Hämeri et al., 2002). However, glutaric, pinonic, adipic acid, and phthalic acids with low water solubility show no influence on the deliquescence behavior of ammonium sulfate (Cruz and Pandis, 2000; Hämeri et al., 2002).

The deliquescence behavior of Mix_urb with 3.04% organic mass fraction is similar to that of pure ammonium sulfate. Its DRH (around $78\pm 1\%$) is slightly lower than that of pure ammonium sulfate (around $79\pm 1\%$).

Mix_mar particles start to take up water at 53% RH and deliquesce completely around 73%. In contrast to pure ammonium sulfate, the lower DRH ($73\%\pm 1\%$) of Mix_mar indicates that ammonium sulfate in the mixture starts to take up some water

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before reaching its deliquescence point. Surprisingly, below 53% RH, Mix_mar which contains 8.75% sodium malonate shows no growth, however, pure sodium malonate gradually takes up water at the whole range of RH (ref. Fig. 1c). A possible explanation is that sodium malonate may be partly enclosed by ammonium sulfate, the dominant component in the mixture, which depresses its water uptake at lower RH.

Mix_bio particles start to absorb water vapor above 20% RH and deliquescent at around 66%. Below its DRH, Mix_bio behaves similarly to those of pure sodium malonate and sodium succinate, i.e., taking up water gradually with increasing RH.

3.2.2 Effect of organic salts on the hygroscopic growth

The differences in growth factors of Mix_urb with low organic mass fraction and ammonium sulfate are not obvious above their DRHs. For Mix_mar and Mix_bio, growth factors above RH = 80% are slightly lower than, but quite close to those of pure ammonium sulfate, as shown in Fig. 2. This is not expected because the non-hygroscopic fraction of ammonium oxalate should depress the water uptake of the mixtures compared to pure ammonium sulfate particles. On this point, a detailed discussion with the help of a modified Köhler theory will be given in the next section.

3.2.3 Comparison with theoretical predictions

The hygroscopic growth of the multi-component particles can be predicted using the Köhler theory proposed by Petters and Kreidenweis (2007). In the Köhler model, the effective hygroscopicity parameter of the mixture, κ , is the summation of hygroscopicity parameter of each component, κ_j :

$$\kappa = \sum_i \varepsilon_i \kappa_i \quad (2)$$

Here, ε_i is the individual (dry) component volume fraction. Mass fractions given in Table 2 are converted to volume fractions using bulk density values, which are also shown

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in the last line of Table 2. Here, i means the number of component in the mixture. κ_i can be derived from the hygroscopic growth factor (Petters and Kreidenweis, 2007):

$$\kappa_i = (g_i^3 - 1) \left(\frac{\exp\left(\frac{A}{D_d g_i}\right) - 1}{RH} - 1 \right) \quad (3)$$

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

5 where g_i is the growth factor of each component. $\sigma_{s/a}$ is the surface tension of water contact with air, 0.0728 N/m at 20 °C. M_w and ρ_w are the molecular weight and density of water, respectively. T and R are temperature and the universal gas constant. D_d is the dry particle diameter, here, 100 nm, and RH is the RH at which the growth factor is measured, here, 90%.

10 The κ -values derived from the growth factors at 90% using Eq. (3) for individual organic salts and ammonium sulfate are given in the last column of Table 1. For the mixtures, the calculated κ based on growth factor at $RH = 90\%$ and predicted κ at this RH using Eq. (2) are shown in Table 3. The agreements of predicted κ values and those calculated based on growth factors for Mix_mar and Mix_urb are within the uncertainty of 1%.

15 For Mix_bio, the predicted κ is significantly lower than the measured one, indicating that κ -Köhler theory underestimate the hygroscopic growths of those mixtures. In Mix_bio, a large fraction of mixture is ammonium oxalate with low water solubility. If its water solubility is taken into account, the Eq. (2) can be presented as (Petters and Kreidenweis, 2008):

$$\begin{aligned} \kappa &= \sum_i \varepsilon_i \kappa_i H(x_i) \\ x_i &= (g^3 - 1)C_i / \varepsilon_i \\ H(x_i) &= \begin{cases} x_i & x_i < 1 \\ 1 & x_i \geq 1 \end{cases} \end{aligned} \quad (5)$$

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Here, g is the growth factor of the mixture. C_i is the solubility of the solute in water, expressed here as volume of compound per unit volume of water. The density and solubility of ammonium oxalate are 1480 kg/m^3 and 44.5 g/kg , respectively. Then, C_i equals to $0.03 \text{ m}^3/\text{m}^3$. The κ of ammonium oxalate used in Eq. (5) is not 0.02, but 0.38, which is calculated according to the growth factor at 94% reported by Mensah et al. (2009) (see Petters and Kreidenweis, 2008). The predicted κ values considering water solubility for all mixtures are given in the last column of Table 1. Apparently, these κ -values are closer to the measured values than those without considering solubility.

4 Summary

The hygroscopic behavior of the atmospherically relevant organic salts and their mixtures with ammonium sulfate are characterized using a H-TDMA in this study. The deliquescence RHs for sodium acetate and sodium pyruvate are around 40% and 82%, respectively. Other organic salts including sodium malonate, sodium succinate, sodium tartrate, ammonium tartrate, sodium maleate, and humic acid sodium salt take up water continuously with increasing RH. No hygroscopic growth is observed for sodium oxalate, while ammonium oxalate shows only a slight growth.

The mixtures of organic salts with ammonium sulfate, which are prepared simulating the atmospheric aerosols, are determined. The results show that organic salts have significant effects on the deliquescence of ammonium sulfate. With increasing organic mass fraction, a clear shift in DRH to lower RH, as well as a smoothing of the deliquescence behavior, is observed. Above 80% RH, the humidograms of mixtures are quite close to that of pure ammonium sulfate. The Köhler theory is used to predict the effective hygroscopicity parameter, κ , for mixtures at RH = 90%. The results show that the modeled κ is lower than those derived from H-TDMA measurement. However, if the water solubility of ammonium oxalate is taken into account, the results show a much better agreement with those derived from H-TDMA measurements.

Acknowledgements. Here, we thank Heike Wex in the cloud group of IfT for the suggestive discussion.

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Table 1. Polynomial coefficients of the growth curve parametrization as well as growth factors (GF) and kappa values at RH = 90%.

Species	RH range	A	B1	B2	B3	B4	R-Square	SD	GF (90%)	κ (90%)
Ammonium sulfate	0.80–0.90	2076.4	−9977.1	17972.8	−14379	4311.8	0.99	0.01	1.70	0.46
Sodium acetate	0.50–0.90	1.26	−4.57	18.68	−26.50	13.45	0.98	0.03	1.79	0.55
Sodium oxalate	0.20–0.90	1	0	0	0	0	0	0	1.00	0.00
Ammonium oxalate	0.30–0.80	0.99	0.38	−1.39	2.06	−1.00	0.92	0.002	1.05	0.02
Sodium malonate	0.20–0.90	1.08	−1.51	7.57	−11.38	6.44	1.00	0.01	1.78	0.55
Sodium succinate	0.20–0.90	1.06	−1.12	6.11	−9.01	4.95	1.00	0.01	1.69	0.45
Sodium tartrate	0.20–0.90	1.05	−0.89	3.82	−5.77	3.66	1.00	0.01	1.54	0.32
Ammonium tartrate	0.20–0.90	1.02	−0.33	1.81	−3.30	2.30	0.99	0.01	1.29	0.14
Sodium pyruvate	0.84–0.90	4387.71	−20241.28	35032.61	−26955.00	7780.72	1.00	0.01	1.70	0.46
Sodium maleate	0.20–0.90	1.07	−1.30	6.58	−9.73	5.55	1.00	0.01	1.78	0.54
Humic acid sodium salt	0.20–0.90	0.99	0.06	0.33	−0.76	0.67	0.99	0.00	1.19	0.09

$$GF = A + B1 \times RH^{(1)} + B1 \times RH^{(2)} + B1 \times RH^{(3)} + B1 \times RH^{(4)}$$

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Table 2. The chemical composition of mixtures, mass percentage, wt%.

No.	Ammonium Sulfate	Ammonium oxalate	Sodium malonate	Sodium succinate	Sodium pyruvic	Sodium maleate
Mix_urb	96.96%	2.39%	0.20%	0.45%	–	–
Mix_mar	78.67%	12.59%	8.75%	–	–	–
Mix_bio	58.28%	28.84%	4.35%	7.67%	0.51%	0.35%
Density [g cm ⁻³]	1.77 ^a	1.50 ^b	1.75 ^c	1.68 ^d	1.54 ^e	1.79 ^f

^a <http://www.jtbaker.com/msds/englishhtml/a6192.htm>;

^{b,c,d,e,f} Peng and Chan (2001).

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Table 3. Growth factors and measured and predicted κ values at RH = 90%.

No.	GF (90%)	κ 90%	Predicted κ (90%)	Predicted κ (solubility 90%)
Mix_urb	1.70±0.04 ^a	0.46±0.04 ^b	0.45	0.45
Mix_mar	1.67±0.04	0.43±0.04	0.40	0.42
Mix_bio	1.64±0.04	0.40±0.04	0.32	0.35

^a The errors are calculated according to the uncertainty in growth factor of 2.5% at 90%.^b The errors are estimated based on the uncertainties in growth factor propagating to κ values.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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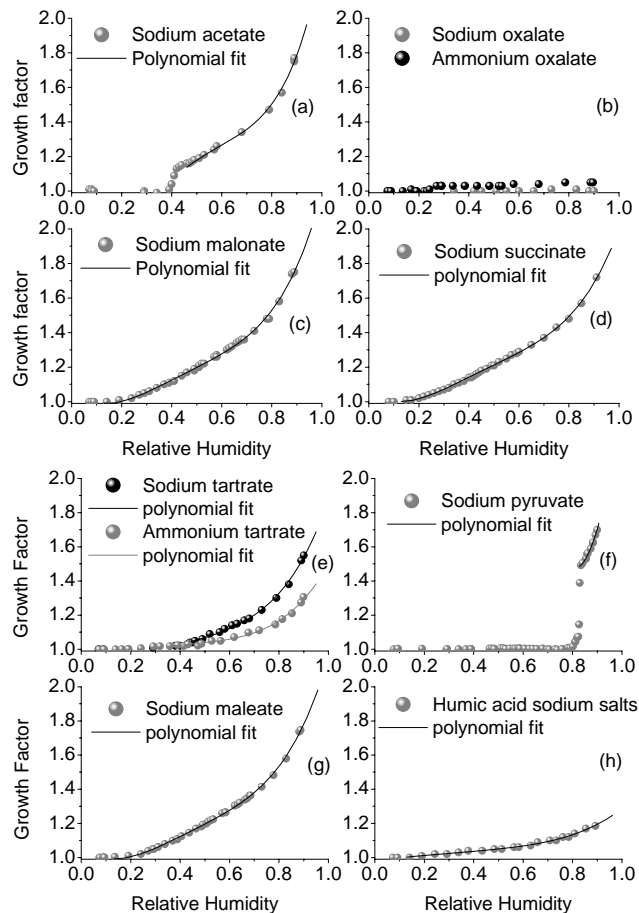
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**Fig. 1.** Hygroscopic growth factors of organic salts as a function of relative humidity.

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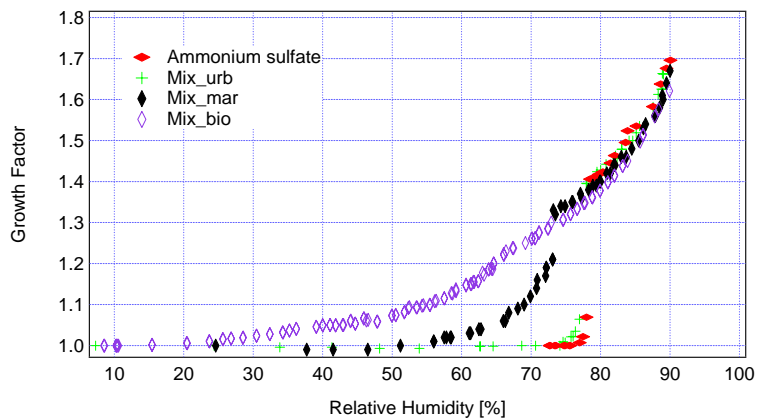


Fig. 2. The growth factors of mixtures and $(\text{NH}_4)_2\text{SO}_4$ versus RH.