



Hygroscopicity of Inorganic Aerosols: Size and Relative Humidity Effects on the Growth Factor

Dawei Hu¹, Liping Qiao¹, Jianmin Chen^{1*}, Xingnan Ye¹, Xin Yang^{1*}, Tiantao Cheng¹, Wen Fang²

¹ *Department of Environmental Science & Engineering, Fudan University, Shanghai 200433, China*

² *Institute of Weather Modification, Chinese Academy of Meteorological Sciences, Beijing 100084, China*

ABSTRACT

The hygroscopic properties of inorganic salt particles, including $(\text{NH}_4)_2\text{SO}_4$, NaCl, Na_2SO_4 and NaNO_3 , are investigated using a self-assembled hygroscopic tandem differential mobility analyzer (H-TDMA) system. The iso-GF (growth factor) curves are derived to illustrate the effects of the initial particle size (D_0) and relative humidity (RH) on the GFs. For those salt particles of 100 nm, the GFs measured agreed well with their theoretical Köhler curves. In the size range of 20–200 nm, the GFs of $(\text{NH}_4)_2\text{SO}_4$, NaCl and Na_2SO_4 particles all continuously decrease with D_0 increasing below the deliquescence RH (DRH). However, when RH is higher than the DRH, the GFs of those salts aerosols increase with D_0 throughout the investigated size range. Similar increase trend of GFs with D_0 is also observed for NaNO_3 aerosols though they do not exhibit the abrupt deliquescence behavior. From iso-GF curves, it can be clearly observed that the GFs of $(\text{NH}_4)_2\text{SO}_4$, NaCl and Na_2SO_4 particles all increase with the RH while the values decrease with D_0 below DRH. And above DRH, the GFs are more sensitive to D_0 for particles smaller than 60 nm, while the GFs are more sensitive to RH for particles larger than 80 nm. For NaNO_3 aerosols, the iso-GF curves indicate the size-effect becomes more prominent on their hygroscopicity as the RH increases. The iso-GF curves provide a lucid and explicit insight into the hygroscopic growth of salts particles. Through iso-GF curves, we can clearly elucidate the major factor that affects the ultimate particle diameter at ambient atmosphere.

Keywords: H-TDMA; Hygroscopicity; Inorganic aerosols; Size-effect; Iso-GF.

INTRODUCTION

The hygroscopic growth of aerosol particles are of current interest due to their effects on light scattering and absorption properties of particles which thereby affect the air quality, visibility, Earth's radiation and the climate (Charlson *et al.*, 1992; IPCC, 2007). On a global basis, sulfates, nitrates and chlorides contribute the largest to the mass budget of fine atmospheric particles (IPCC, 2007; Li *et al.*, 2009; Shen *et al.*, 2009). These inorganic salt aerosols are hygroscopic by nature, thus their size, phase and subsequently the optical properties would be strongly influenced by the ambient relative humidity (RH). Based on recent studies, the effect of sulfate particles on the annual-average global direct radiative forcing, arising from the fluctuation of atmospheric particles between aqueous and solid state, is estimated up to as much

as 24% (Martin *et al.*, 2004; Wang *et al.*, 2008a, 2008b). Thus, close attention has been paid to study the hygroscopic properties of these inorganic salts.

Hygroscopic tandem differential mobility analyzer (H-TDMA) is a common approach to study the hygroscopic properties and phase transitions of atmospheric particles (Liu *et al.*, 1978). Through H-TDMA, primarily hygroscopic growth factors (GFs) are measured, and information about particle phase and phase transitions can be inferred as a derived quantity. Previous works on determining the deliquescence transitions and water content of single salt particles, including sulfates ($(\text{NH}_4)_2\text{SO}_4$), chlorides (NaCl) and nitrates (NaNO_3 , $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$), are mainly concentrated on that of initial diameter of 100 nm (Cruz *et al.*, 2002; Gysel *et al.*, 2002; Gibson *et al.*, 2006). In general, those sulfates and chlorides particles exhibit pronounced deliquescence behavior in humid air, i.e. their phases remain unchanged until RH reaches the deliquescence RH (DRH), from which they deliquesce abruptly to form a saturated solution droplet by water vapor condensation (Gysel *et al.*, 2002). Otherwise, those nitrates particles which are highly hygroscopic, always gain their water content smoothly at ambient conditions (Gibson *et al.*, 2006). Recently, initial

* Corresponding authors. Tel.: +86-21-65642521;
Fax: +86-21-65642080
E-mail address: jmchen@fudan.edu.cn,
yangxin@fudan.edu.cn

particle sizes for hygroscopicity studies have been developed to a wide-size-scale, ranged mainly from 6 to 200 nm. The hygroscopic properties of salts particles are revealed to be initial particle size dependent. Biskos *et al.* (2006) found from the hygroscopic properties of 6 to 60 nm NaCl particles that the GFs steadily decreased with decreasing dry particle size below approximately 40 nm at the RH above deliquescence point. Such size-dependent hygroscopic properties of NaCl particles are also demonstrated by Park *et al.* (2009). Moreover, Russel *et al.* (2002) proved the similar size-dependent hygroscopic properties of NaCl particles through model calculations. However, the size-dependent hygroscopic properties varied a lot from various chemical species. For atomizer-generated KCl, MgCl₂ and CaCl₂ particles, their GFs are independent from particle size, while distinct size-effect on GFs for atomizer-generated (NH₄)₂SO₄ particles is observed by Park *et al.* (2009).

Although some efforts have been made to investigate the size-effect of salts particles on hygroscopic properties, still some chemical species being ubiquitous in aerosol particles (such as NaNO₃ and Na₂SO₄) are not taken into consideration. Moreover, since both the size-effect and RH may greatly impact on the GFs, it will be of significance to distinguish the dominant factor from size-effect and RH. To our knowledge, it is still less details till now to distinguish the impact of size-effect and RH on the GF of inorganic aerosols. To consider the impact of size-effect and RH synchronous will provide a new insight into visibility degradation and air quality improvement under ambient atmospheric condition.

In this paper, the hygroscopic properties of several salts particles, (NH₄)₂SO₄, NaCl, Na₂SO₄ and NaNO₃ included, are investigated using H-TDMA technique. And the iso-GF curves are put forward to differentiate the impact of size-effect and RH.

EXPERIMENTAL PROCEDURE

The experimental setup consists of an aerosol generator and a set of H-TDMA system (Fig. 1). The setup has been described in detail in a previous paper (Ye *et al.*, 2009). Herein, a brief description of the experimental procedure is presented. Aerosol particles, produced by the aerosol generator (Model 3076, TSI Inc., USA), are firstly dried to a low RH (RH < 5%) and then fed into the first differential mobility analyzer (DMA-1). Through DMA-1, particles of a certain “dry” size are selected. Afterward, the size-selected-particles are exposed to a controlled humid environment, i.e. a multitube Nafion humidifier (Models PD-70T-24ss, Perma Pure Inc.) where RH is regulated in the range of 5% to 90%. Then, a new particle size distribution is measured by the second DMA (DMA-2) with combination of a Condensation Particle Counter (CPC, Model 3771, TSI Inc., USA). And hygroscopic GFs (D_p/D_0), defined as the ratio of the humidified (D_p) and dry particle mobility diameter (D_0), could be deduced. In this system, to avoid unwanted particle dehydration or further hygroscopic growth in DMA-2, the RH is monitored both on the inlet and outlet of DMA-2 with RH modules (Model HMM22D Module,

Vaisala Inc.) to make sure the RH difference between the humidified sample and the humidified DMA-2 sheath gas flow is within 1% RH (throughout all the RH range). Both the DMA-1 and DMA-2 are operated with N₂ as sheath gas in 6.5 LPM, and with sample in 1.0 LPM. The particle size mainly covered the range of 10–400 nm. The accuracy of all DMAs is tested using the standard PSL particles, and the test experiment of H-TDMA system is described in detail elsewhere (Ye *et al.*, 2009).

In this study, the elevated-RH is selected as 20%, 30%, 40%, 50%, 60%, 70%, 80%, 82%, 84%, 86% and D_0 is selected as 20, 40, 60, 80, 100, 120, 140, 160, 180, 200 nm, respectively. Meantime, to better ascertain the DRH of (NH₄)₂SO₄ and NaCl aerosols, the GFs of 100 nm (NH₄)₂SO₄ at 78% RH and 100 nm NaCl at 73%, 75%, 78% RH are also measured. For accuracy, each experiment is repeated 5 times at least.

RESULTS AND DISCUSSION

Hygroscopic Growth of $D_0=100$ nm (NH₄)₂SO₄, NaCl, Na₂SO₄ and NaNO₃ Aerosols

Firstly, experiments with (NH₄)₂SO₄ are performed to test the H-TDMA system. The hygroscopic properties of (NH₄)₂SO₄ have been well understood and characterized by several different techniques (Tang and Munkelwitz, 1993, 1994; Tang *et al.*, 1995; Cziczo *et al.*, 1997; Onasch *et al.*, 1999; Gysel *et al.*, 2002), and thus making it an ideal system to test the H-TDMA system. Fig. 2(a1) presents a series of Gaussian fits to the measured size distributions of 100 nm (NH₄)₂SO₄ aerosols as a function of RH. The fits have been normalized to the peak concentration. It shows that there is no shift in diameter until the DRH is reached, at which point there is a distinct and abrupt increase in size of the particles as the particles undergo a solid to liquid phase transition. Fig. 2(b1) displays the measured hygroscopic growth curve of 100 nm (NH₄)₂SO₄ aerosols. A good agreement is observed between the measured GFs and the theoretical Köhler curves (derived from AIM model). And the measured DRH appears at $80 \pm 2\%$ RH, also in good agreement with values reported previously (Tang and Munkelwitz, 1993; Onasch *et al.*, 1999; Gysel *et al.*, 2002).

The hygroscopic behavior of $D_0=100$ nm NaCl, Na₂SO₄ and NaNO₃ aerosols are displayed in Fig. 2(a2–a4). Fig. 2(a2) shows that NaCl aerosols have a deliquescence point like (NH₄)₂SO₄ and occur at $75 \pm 2\%$ RH at 25°C, agree well with the values reported previously (Tang and Munkelwitz, 1993). Moreover, as the measured hygroscopic growth curve of NaCl aerosols shows in Fig. 2(b2), good agreement is also observed between the GFs and theoretical hygroscopic curve. For Na₂SO₄ aerosols, as can be seen from Fig. 2(a3), crystalline Na₂SO₄ particles remain unchanged until RH reaches the DRH. Then, they deliquesce spontaneously to form a saturated solution droplet by water vapor condensation, gain about 1.7 times its initial diameter. After that, the droplets continue to grow as RH further increases. The hygroscopic properties of Na₂SO₄ aerosols have been examined previously with several different techniques and are expected to deliquesce at 84% RH at 25°C

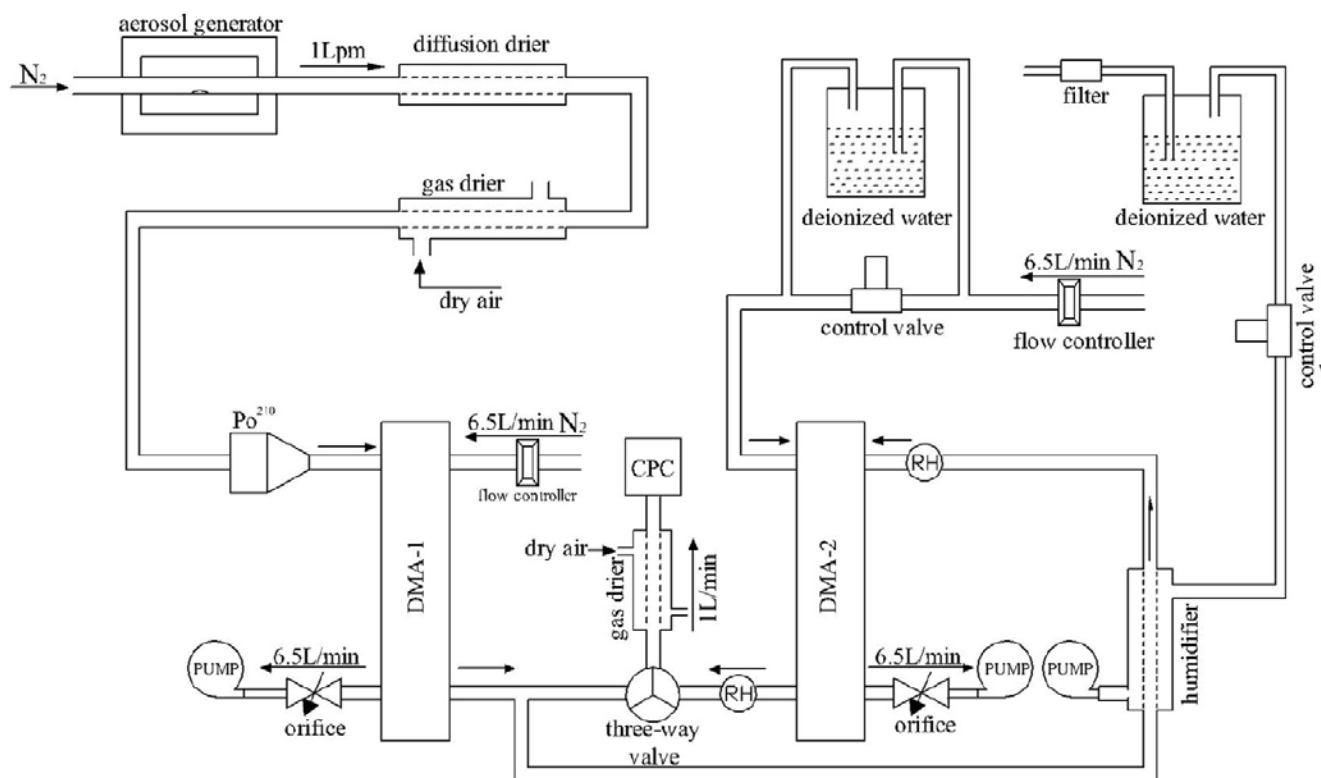


Fig. 1. Schematic diagram of the H-TDMA system.

(Tang and Munkelwitz, 1994). As Fig. 2(b3) displays, the measured DRH of Na_2SO_4 aerosols appeared at $82 \pm 2\%$ RH, a little lower than the values expected. Such discrepancy may be caused by the slight temperature fluctuates during the experiment where the temperature increase will lead to the decrease of DRH (Tang and Munkelwitz, 1993).

As Fig. 2(a4) presents, unlike $(\text{NH}_4)_2\text{SO}_4$, the NaNO_3 aerosols do not exhibit the deliquescence phenomenon and show continuous growing with RH increasing in this experiment. Literature data (Tang and Munkelwitz, 1994) reported a hysteresis effect of NaNO_3 particles at 25°C with a DRH of 74.5%, and an ERH between 30% and 0.05%. The minimum RH in this experiment (about 5% after the diffusion dryer) is obviously not low enough for the spontaneous crystallization of the NaNO_3 particles. Thus, NaNO_3 aerosols do not completely dry out even at 5% RH. Because of the missing crystallization, the NaNO_3 aerosols in the DMA-1 have a diameter larger than the volume equivalent diameter of the solute NaNO_3 . Thus, the particle diameter measured in the DMA-1 (RH = 5%) should be divided by the theoretical GF at this RH (1.02 at 25°C and 5% RH) to deduce the real diameter D_0 (98 nm) of dry NaNO_3 aerosols. Fig. 2(b4) displays the measured GFs curve and it agrees well with the theoretical hygroscopic growth curve.

Size-effect on the Growth Factor

$(\text{NH}_4)_2\text{SO}_4$, NaCl and Na_2SO_4 aerosols all exhibit pronounced deliquescence behavior, and their growth factors as a function of D_0 are demonstrated in Fig. 3. As can be

seen, below DRH, the GFs of those salt aerosols all continuously decrease with D_0 increasing in the range from 20 to 200 nm at given RH, and the smallest particles show the highest growth factor. Take $(\text{NH}_4)_2\text{SO}_4$ aerosols for instance, the GFs decrease from 1.05 for 20 nm aerosols to 1.03 for 200 nm aerosols at 70% RH. However, the theoretical GFs of those inorganic salt particles should be 1.00 below DRH. This interesting finding can be explained from two aspects. On the one hand, the small particle growth just below the DRH is probably caused by water adsorption on particle surface. Several studies (Dia *et al.*, 1997; Romakkaniemi *et al.*, 2001) have testified that the salt surfaces are actually adsorbed by water even though the ambient RH was far below its deliquescence point. On the other hand, although the adsorption of water vapor on small particles is more difficult than that on large particles due to the curvature effect, the relative increment (expressed by GFs) of small particles is still higher than large particles as a result of their high surface to volume ratio. In addition, it is noteworthy that the GF-Size curves gradually lift up with increasing of RH. Probably higher RH that means more moisture in the atmosphere leads the particles to adsorb more water vapor on particle surface.

When RH is higher than the deliquescence point, the GFs of those salts aerosols increase with D_0 throughout the investigated size range. Further analyses reveal the GFs increase pronouncedly for particles in the range of 20–100 nm, and the increase trend relatively slows down for particles in the range of 100–200 nm. As Fig. 3(b1) shows, the GFs increase from 1.52 for 20 nm $(\text{NH}_4)_2\text{SO}_4$ aerosols to 1.61 for 100 nm aerosols at 86% RH, corresponding to

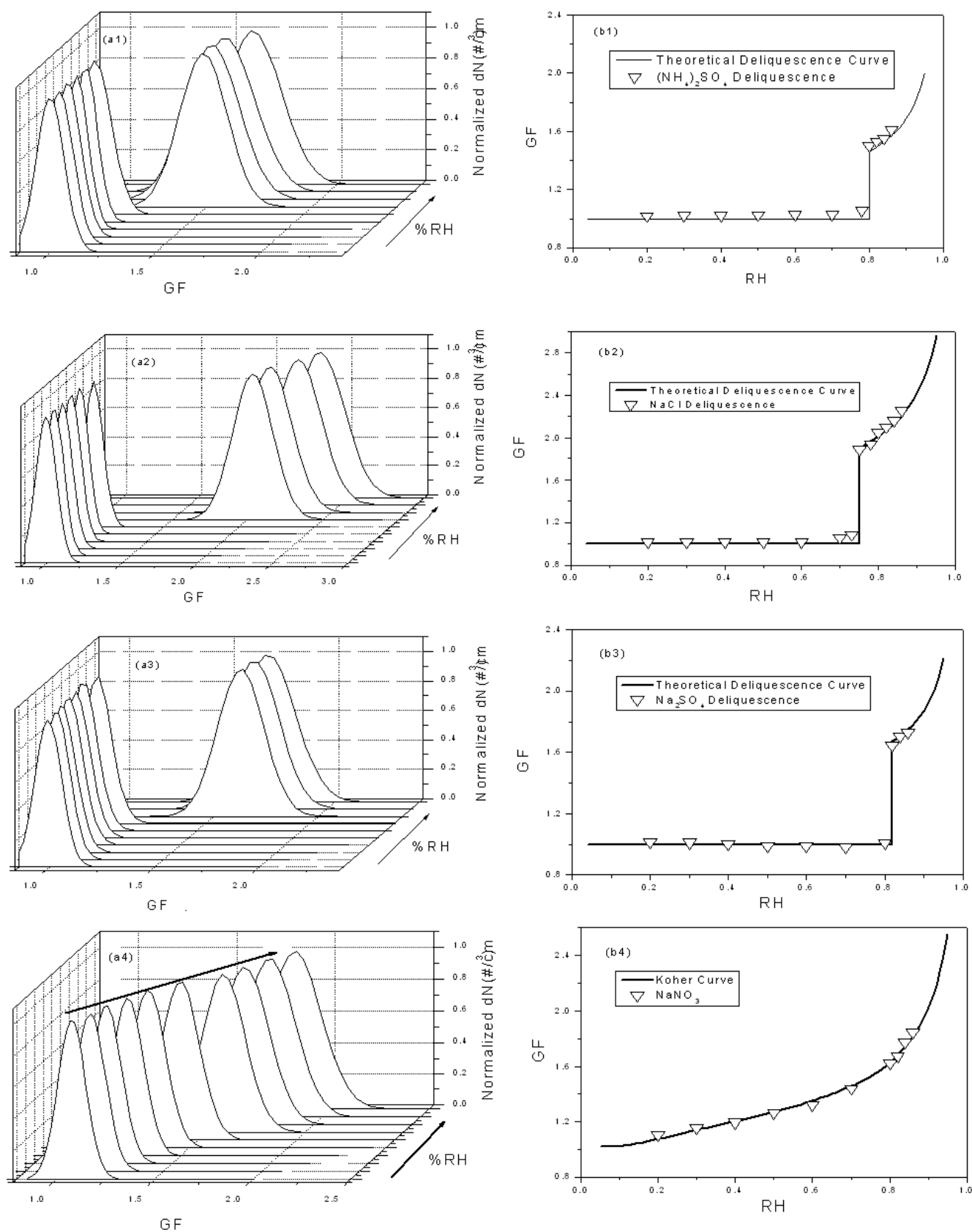


Fig. 2. Hygroscopic growth of $D_0 = 100$ nm: (a1) $(\text{NH}_4)_2\text{SO}_4$, (a2) NaCl, (a3) Na_2SO_4 , (a4) NaNO_3 as a function of RH. The distributions displayed by Gaussian fitting and normalized to the peak concentration. The growth factor of $D_0 = 100$ nm: (b1) $(\text{NH}_4)_2\text{SO}_4$, (b2) NaCl, (b3) Na_2SO_4 , (b4) NaNO_3 as a function of increasing (∇) RH. The solid line represents the theoretical deliquescence curve as calculated from Köhler theory.

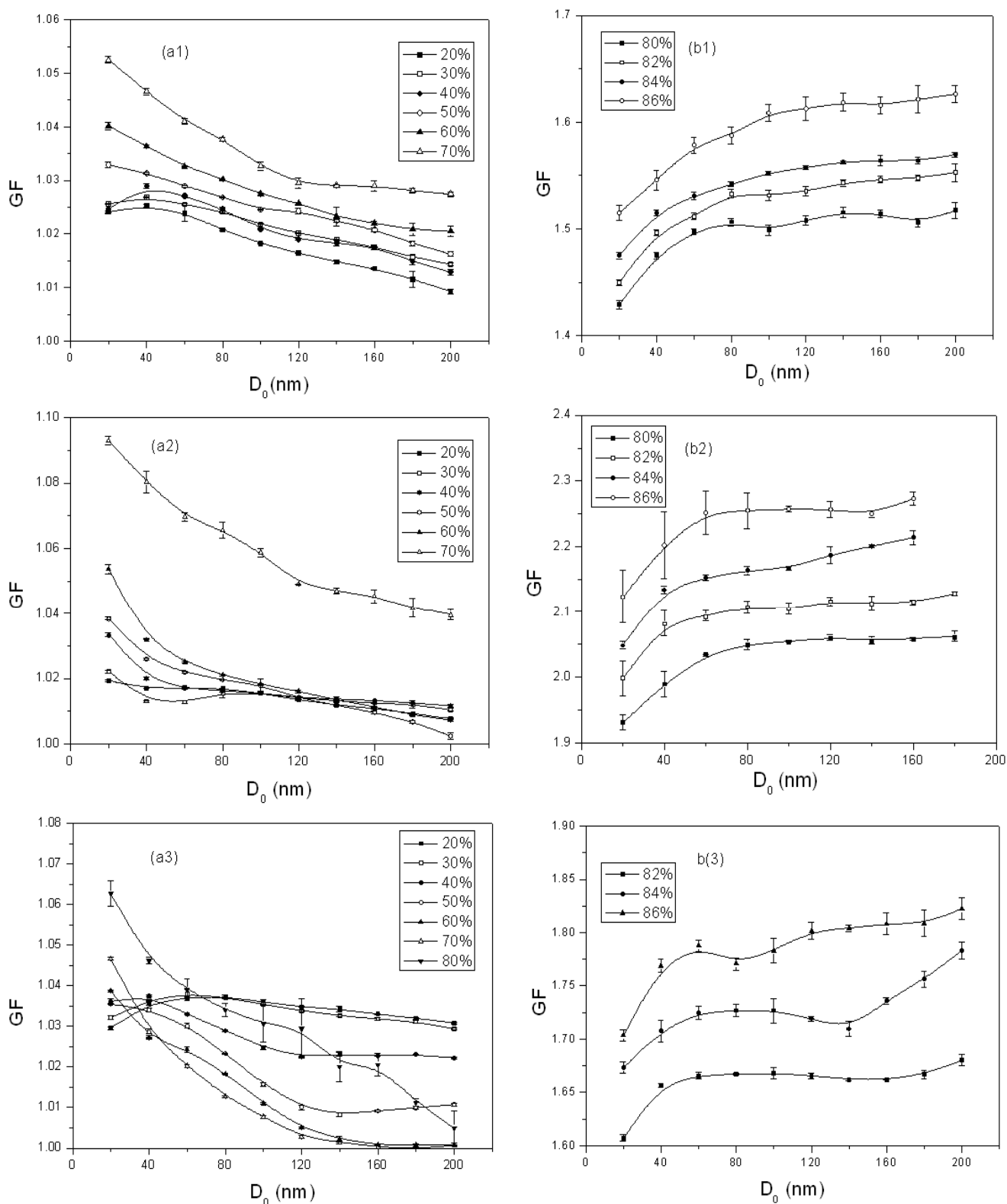


Fig. 3. The growth factor as a function of initial particle size of: (a1) $(\text{NH}_4)_2\text{SO}_4$, (a2) NaCl, (a3) Na_2SO_4 aerosols at the RH below deliquescence point; (b1) $(\text{NH}_4)_2\text{SO}_4$, (b2) NaCl, (b3) Na_2SO_4 aerosols at the RH above deliquescence point.

0.09 GF increment, while it only increases by 0.02 for aerosols from 100 to 200 nm. Moreover, the diameter increments (Table 1) are corresponded to 10.3, 60.9 and 125.3 nm for those $(\text{NH}_4)_2\text{SO}_4$ aerosols of 20, 100 and 200

nm, respectively. It indicates that the large particles are hygroscopic vulnerably and gaining water easier. This might be caused by the fact that larger particles contain relatively more solute than smaller ones.

Table 1. The diameter increment of (NH₄)₂SO₄, NaCl, Na₂SO₄ and NaNO₃ aerosols at different RH conditions.

Compounds	Original Particle Diameter D ₀ (nm)	D _p -D ₀ value (nm)									
		20%	30%	40%	50%	60%	70%	80%	82%	84%	86%
(NH ₄) ₂ SO ₄ (DRH=80%)	20	0.5	0.5	0.5	0.7	0.8	1.1	8.6	9.0	9.5	10.3
	40	1.0	1.1	1.2	1.3	1.5	1.9	19.0	19.9	20.6	21.8
	60	1.4	1.5	1.6	1.7	2.0	2.5	29.8	30.7	31.9	34.7
	80	1.7	1.9	2.0	2.1	2.4	3.0	40.5	42.6	43.3	47.0
	100	1.8	2.2	2.1	2.5	2.7	3.3	49.9	53.1	55.2	60.9
	120	2.0	2.4	2.3	2.9	3.1	3.5	61.0	64.3	66.9	73.5
	140	2.1	2.6	2.6	3.1	3.3	4.1	72.2	76.0	78.8	86.6
	160	2.2	2.8	2.8	3.3	3.5	4.6	82.3	87.4	90.3	98.5
	180	2.1	2.8	2.7	3.3	3.7	5.0	91.1	98.6	101.6	111.9
	200	1.8	2.9	2.6	3.3	4.1	5.5	103.5	110.6	113.9	125.3
NaCl (DRH = 75%)	20	0.4	0.4	0.7	0.8	1.1	1.9	18.6	20.0	21.0	22.5
	40	0.7	0.5	0.8	1.0	1.3	3.2	39.6	43.3	45.4	48.1
	60	1.0	0.8	1.0	1.3	1.5	4.2	62.0	65.6	69.2	75.1
	80	1.4	1.2	1.3	1.6	1.7	5.2	84.0	88.6	93.1	100.4
	100	1.5	1.5	1.6	1.8	1.8	5.9	105.4	110.5	116.7	125.8
	120	1.6	1.7	1.7	1.7	1.9	5.9	127.2	134.0	142.5	150.8
	140	1.7	1.9	1.9	1.7	1.9	6.6	147.8	155.8	168.1	175.0
	160	1.8	2.0	2.1	1.5	1.8	7.3	169.4	178.5	194.3	203.7
	180	1.7	2.2	2.3	1.2	1.6	7.5	191.1	203.2	–	–
	200	1.6	2.1	2.3	0.5	1.5	7.9	–	–	–	–
Na ₂ SO ₄ (DRH = 84%)	20	0.6	0.6	0.7	0.7	0.8	0.9	1.3	12.1	13.5	14.1
	40	1.4	1.5	1.5	1.4	1.1	1.1	1.8	26.3	28.3	30.7
	60	2.2	2.3	2.0	1.8	1.5	1.2	2.3	39.9	43.5	47.3
	80	3.0	3.0	2.3	1.9	1.5	1.0	2.7	53.4	58.2	61.7
	100	3.6	3.5	2.5	1.6	1.1	0.8	3.1	66.8	72.7	78.3
	120	4.2	4.1	2.7	1.2	0.6	0.3	3.5	79.9	86.3	96.2
	140	4.8	4.6	3.2	1.2	0.3	0.2	2.8	92.7	99.3	112.6
	160	5.3	5.1	3.6	1.5	0.1	0.0	3.3	106.0	117.8	129.4
	180	5.8	5.6	4.1	1.8	0.1	0.0	2.0	120.1	136.1	145.5
	200	6.2	5.9	4.4	2.2	0.2	0.1	1.0	136.1	156.6	164.5
NaNO ₃ (No observed DRH)	19.6	2	3	3.5	4.6	5.6	7.5	9.9	10.5	11.7	12.8
	39.2	4.2	6.4	7.5	10	12.4	16.9	23.1	24.7	27.3	30.6
	58.8	6.5	9.4	11.5	15.1	19	26	36.1	38.9	43.4	48.6
	78.4	8.5	12.5	15.6	20.4	25.5	34.9	48.9	53	60.5	65.5
	98	10.3	15.3	18.9	25.5	31.5	43.2	61.3	66.5	76.3	83.4
	117.6	12	18.2	22.5	30.3	38.8	52.1	73.6	80.3	92.8	100.9
	137.3	13.7	21	26.4	35.1	45.3	60.6	85.4	95.3	103.4	118.9
	156.9	15.4	23.6	30.2	40.1	51.9	69.1	99.8	108.1	118.7	137.9
	176.5	17.2	26.3	33.7	44	58.5	77	113.8	122.9	135.2	161.4
	196.1	18.7	28.6	37.2	48.5	65.5	85.2	127.6	139.7	151.1	174.9

Our results consist with the size-dependent hygroscopicity reported in the previous works (Gysel *et al.*, 2002; Biskos *et al.*, 2006; Park *et al.*, 2009). Kelvin effect is supposed to be the major reason caused the size-dependent GFs. The growth of aqueous droplets in humid air is commonly described by Köhler theory (Köhler, 1936; Gysel *et al.*, 2002; Kreidenweis *et al.*, 2005). At equilibrium, the RH is the ratio of the vapor pressure over a solution droplet to the saturation vapor pressure of water. The relationship between droplet

diameter and RH at equilibrium is given by:

$$RH = a_w C_{ke} = a_w \exp\left(\frac{4v_w \sigma_{sol/v}}{RTD_p}\right) \quad (1)$$

where a_w is the water activity, C_{ke} is the Kelvin correction factor, v_w is the partial molar volume of water, $\sigma_{sol/v}$ is the surface tension of the solution at the composition of the droplet, R is the universal gas constant, T is the

temperature and D_p is the equilibrium diameter. The Köhler equation states that the RH equals the water activity for a plane solution surface, and that for curved surfaces such as aerosol particles, the water activity is always smaller than the ambient RH. The Kelvin factor therefore causes the hygroscopic growth to decrease with decreasing dry size for particles of identical composition. Water-soluble aerosol particles grow by condensation of water vapor simply because the water activity of the aqueous solution strives to equilibrate to the RH in the surrounding air in accordance with the Köhler equation.

Among the salts investigated, the abrupt deliquescence behavior do not occurred for the NaNO_3 aerosols. Like the hygroscopic growth behaviors of $(\text{NH}_4)_2\text{SO}_4$, NaCl and Na_2SO_4 above DRH, similar increase trends of GFs with particle size are also observed for NaNO_3 aerosols (Fig. 4). Throughout the entire RH scope, the GFs keep increasing markedly until D_0 reaches 100 nm, and the increase trend of the GFs slows down as the particles further increasing. At 60% and 86% RH, the GFs increase from 1.28 and 1.65 for $D_0 = 20$ nm particles to 1.32 and 1.85 for $D_0 = 100$ nm particles, and ultimately the values increase to 1.33 and 1.89 for $D_0 = 200$ nm NaNO_3 aerosols, respectively.

Size and Relative Humidity Effects on the Growth Factor

The GFs of aerosols are influenced markedly not only by their chemical composition, but also by the initial particle size and ambient RH. To distinguish the dominant impact on GFs from size-effect and RH, iso-GF curves with D_0 and RH as the coordinates are put forward and the corresponding curves of $(\text{NH}_4)_2\text{SO}_4$, NaCl and Na_2SO_4 aerosols are illustrated in Fig. 5. Below DRH, the GFs increase with RH while they decrease with D_0 . It indicates RH plays a dominant role to augment the particle diameter at ambient atmosphere. Above DRH, the GFs are more sensitive to particle size for particles smaller than 60 nm, while the GFs are more sensitive to RH for particles larger than 80 nm. For NaNO_3 aerosols (Fig. 6), at $80\% \leq \text{RH} \leq$

86%, the GFs are easier to increase with D_0 for particles smaller than 60 nm, while they are easier to increase with RH for particles larger than 80 nm. However, at $20\% \leq \text{RH} \leq 70\%$, it is noted that the GFs are more sensitive to the RH than to D_0 even though the particles are smaller than 60 nm. It indicates that the size-effect of NaNO_3 aerosols on their hygroscopicity becomes more and more prominent as the RH increases.

CONCLUSION

Based on the hygroscopicity investigation of $(\text{NH}_4)_2\text{SO}_4$, NaCl , Na_2SO_4 and NaNO_3 aerosols, the size-effect is found on the GFs of Na_2SO_4 and NaNO_3 aerosols besides $(\text{NH}_4)_2\text{SO}_4$ and NaCl aerosols (Gysel *et al.*, 2002; Biskos *et al.*, 2006; Park *et al.*, 2009). Nevertheless, much more studies are needed to explore the size-dependent hygroscopicity of other compounds being ubiquitous in atmospheric aerosols and to elucidate the mechanisms causing such size-effect. As is observed in our studies, The GFs and ultimate particle size are strongly influenced by D_0 . And they will subsequently affect the optical properties of particles which will further impact on Earth's radiation and the climate. In this paper, the iso-GF curves are proposed for the first time. Such iso-GF curves provide a lucid and explicit insight into the hygroscopic growth of salts particles. Through iso-GF curves, we can clearly determine the major factor that affects the ultimate particle diameter at ambient atmosphere. Then, it will be of significance to improve the visibility and air quality by controlling the dominant factor impact on aerosol hygroscopicity.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (Nos. 40575073, 40533017, 40605001, 40728006, 40775080 and 40875053), the National Key

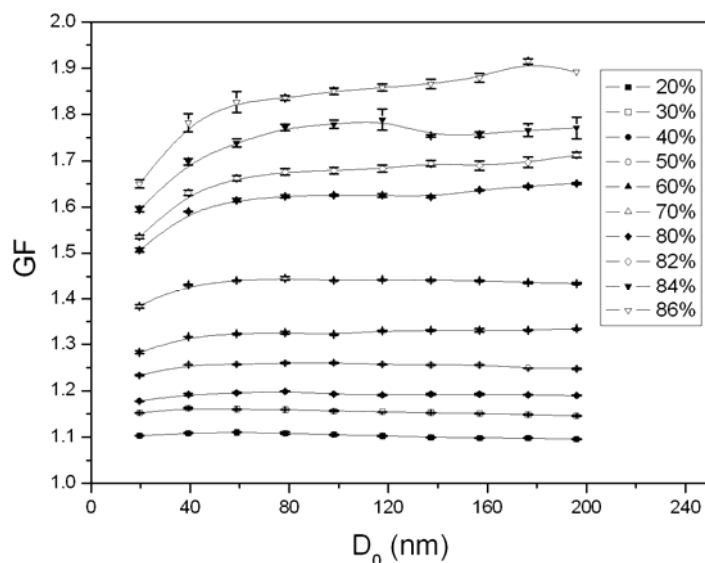


Fig. 4. The growth factor as a function of initial particle size of NaNO_3 aerosols.

Technology R&D program (No. 2006BAC12B001) of China, the Key Science & Technology Project (No. 108050) from the Chinese Ministry of Education and the

International Collaboration Project from the Science and Technology Commission of Shanghai Municipality (No. 09160707700).

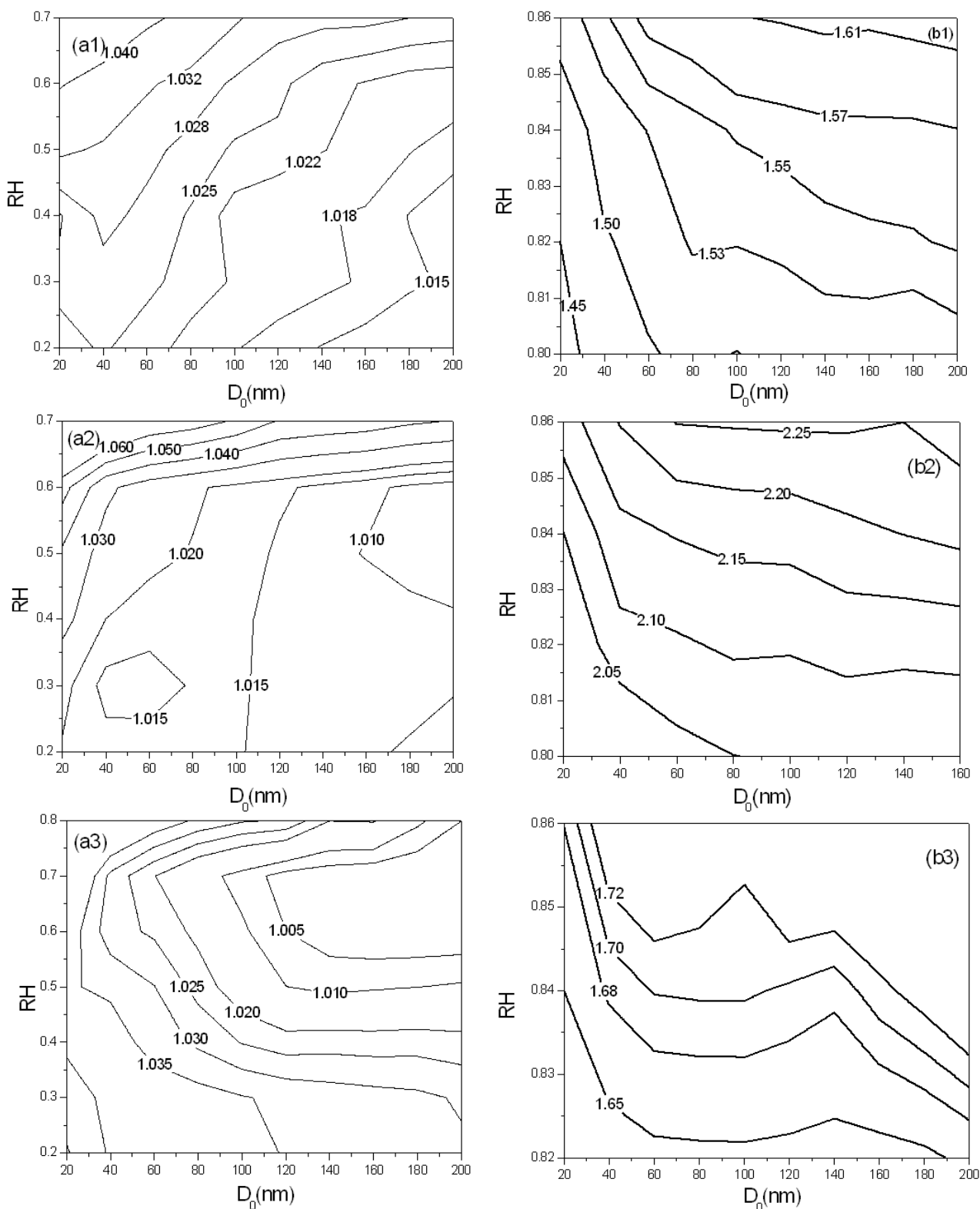


Fig. 5. The relationship among growth factor, RH and particle diameter of: (a1) $(\text{NH}_4)_2\text{SO}_4$, (a2) NaCl, (a3) Na_2SO_4 particles at the RH below deliquescence point; (b1) $(\text{NH}_4)_2\text{SO}_4$, (b2) NaCl, (b3) Na_2SO_4 particles at the RH above deliquescence point.

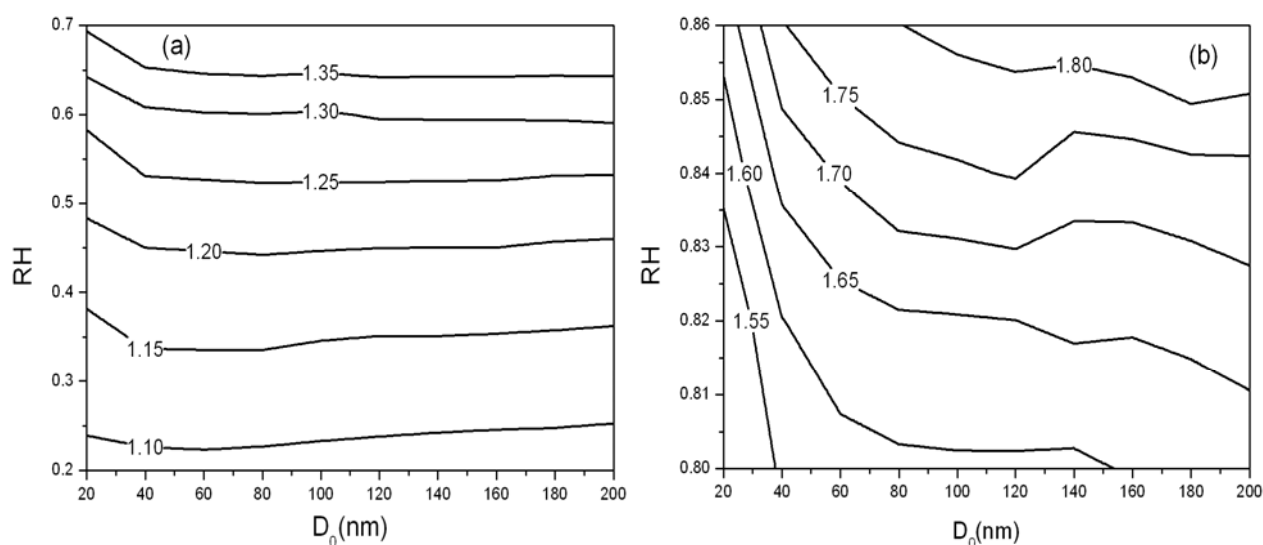


Fig. 6. The relationship among growth factor, RH and particle diameter of NaNO_3 particles: (a) $20\% \leq \text{RH} \leq 70\%$, (b) $80\% \leq \text{RH} \leq 86\%$.

REFERENCES

- Biskos, G., Russell, L.M., Buseck, P.R. and Martin S.T. (2006). Nanosize Effect on the Hygroscopic Growth Factor of Aerosol Particles. *Geophys. Res. Lett.* 33: L07801. doi: 10.1029/2005GL025199.
- Charlson, R.J., Schwartz, S.E., Hales, J.M., Cess, R.D., Coakley, J.A., Hansen, J.E. and Hofmann, D.J. (1992). Climate Forcing by Anthropogenic Aerosols. *Science*. 255: 423–430.
- Cruz, C.N., and Pandis, S.N. (2002). Deliquescence and Hygroscopic Growth of Mixed Inorganic-organic Atmospheric Aerosol. *Environ. Sci. Technol.* 34: 4313–4319.
- Cziczo, D.J., Nowak, J.B., Hu, J.H. and Abbatt, J.P.D. (1997). Infrared Spectroscopy of Model Tropospheric Aerosols as a Function of Relative Humidity: Observation of Deliquescence and Crystallization. *J. Geophys. Res.* 102: 18843–18850.
- Dai, Q., Hu, J. and Salmeron, M. (1997). Adsorption of Water on NaCl (100) Surfaces: Role of Atomic Steps. *J. Phys. Chem. B*. 101: 1994–1998.
- Gibson, E.R., Hudson P.K. and Grassian V.H. (2006). Physicochemical Properties of Nitrate Aerosols: Implications for the Atmosphere. *J. Phys. Chem. A*. 110: 11785–11799.
- Gysel, M., Weingartner, E. and Baltensperger, U. (2002). Hygroscopicity of Aerosol Particles at Low Temperatures. 2. Theoretical and Experimental Hygroscopic Properties of Laboratory Generated Aerosols. *Environ. Sci. Technol.* 36: 63–68.
- IPCC (2007). Climate Change 2007: The Scientific Basis. In Solomon, S., Ding, Y., Griggs, D.G., Noguera, M., Vanderlinden, P.G., Dai, X., Maskell, K. and Johnson, C.A. (Eds). Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press. Cambridge.
- Kohler, H. (1936). The Nucleus in and the Growth of Hygroscopic Droplets. *Trans. Faraday Soc.* 32: 1152–1161.
- Kreidenweis, S.M., Koehler, K., DeMott, P.J., Prenni, A.J., Carrico, C. and Ervens, B. (2005). Water Activity and Activation Diameters from Hygroscopicity Data - Part I: Theory and Application to Inorganic Salts. *Atmos. Chem. Phys.* 5: 1357–1370.
- Li, W.F., Bai, Z.P., Liu, A.X., Chen, J. and Chen, L. (2009). Characteristics of Major $\text{PM}_{2.5}$ Components during Winter in Tianjin, China. *Aerosol Air Qual. Res.* 9: 105–119.
- Liu, B.Y.H., Pui, D.Y.H., Whitby, K.T., Kittelson, D.B., Kousaka, Y. and McKenzie, R.L. (1978). Aerosol Mobility Chromatograph - New Detector for Sulfuric-Acid Aerosols. *Atmos. Environ.* 12: 99–104.
- Martin, S.T., Hung, H.M., Park, R.J., Jacob, D.J., Spurr, R.J.D., Chance, K.V. and Chin, M. (2004). Effects of the Physical State of Tropospheric Ammonium-Sulfate-Nitrate Particles on Global Aerosol Direct Radiative Forcing. *Atmos. Chem. Phys.* 4: 183–214.
- Onasch, T.B., Siefert, R.L., Brooks, S.D., Prenni, A.J., Murray, B., Wilson, M.A. and Tolbert, M.A. (1999). Infrared Spectroscopic Study of the Deliquescence and Efflorescence of Ammonium Sulfate Aerosol as a Function of Temperature. *J. Geophys. Res.* 104: 21317–21326.
- Park, K., Kim, J.S. and Miller, A.L. (2009). A Study on Effects of Size and Structure on Hygroscopicity of Nanoparticles using a Tandem Differential Mobility Analyzer and TEM. *J. Nanopart. Res.* 11: 175–183.
- Romakkaniemi, S., Hameri, K., Vakeva, M. and Laaksonen, A. (2001). Adsorption of Water on 8–15 nm NaCl and $(\text{NH}_4)_2\text{SO}_4$ Aerosols Measured using an Ultrafine Tandem Differential Mobility Analyzer. *J. Phys. Chem. A*. 105: 8183–8188.
- Russell, L.M. and Ming, Y. (2002). Deliquescence of Small Particles. *J. Chem. Phys.* 116: 311–321.

- Shen, Z.X., Cao, J.J., Tong, Z., Liu, S.X., Reddy, L.S.S., Han, Y.M., Zhang, T. and Zhou, J. (2009). Chemical Characteristics of Submicron Particles in Winter in Xi'an. *Aerosol Air Qual. Res.* 9: 80–93.
- Tang, I.N. and Munkelwitz, H.R. (1993). Composition and Temperature-dependence of the Deliquescence Properties of Hygroscopic Aerosols. *Atmos. Environ.* 27: 467–473.
- Tang, I.N., Fung, K.H., Imre, D.G. and Munkelwitz, H.R. (1995). Phase- Transformation and Metastability of Hygroscopic Microparticles. *Aerosol Sci. Technol.* 23: 443–453.
- Tang, I.N. and Munkelwitz, H.R. (1994). Water Activities, Densities, and Refractive Indices of Aqueous Sulfates and Sodium Nitrate Droplets of Atmospheric Importance. *J. Geophys. Res.* 99: 18801–18808.
- Wang, J., Hoffmann, A.A., Park, R.J., Jacob, D.J. and Martin, S.T. (2008a). Global Distribution of Solid and Aqueous Sulfate Aerosols: Effect of the Hysteresis of Particle Phase Transitions. *J. Geophys. Res.* 113: D11206. doi: 10.1029/2007JD009367
- Wang, J., Jacob, D.J. and Martin S.T. (2008b). Sensitivity of Sulfate Direct Climate Forcing to the Hysteresis of Particle Phase Transitions. *J. Geophys. Res.* 113: D11207. doi: 10.1029/2007JD009368.
- Ye, X.N., Chen, T.Y., Hu, D.W., Yang, X., Chen, J.M., Zhang, R.Y., Khakuziv, A.F. and Wang, L. (2009). A Multifunctional HTDMA System with a Robust Temperature Control. *Adv. Atmos. Sci.* 26: 1235–1240.

Received for review, December 2, 2009

Accepted, January 20, 2010