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Mass transfer effects in hygroscopic measurements of aerosol particles

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Abstract. The tandem differential mobility analyzer (TDMA) has been widely utilized to measure the hygroscopicity of laboratory-generated and atmospheric submicrometer particles. An important concern in investigating the hygroscopicity of the particles is if the particles have attained equilibrium state in the measurements. We present a literature survey to investigate the mass transfer effects in hygroscopicity measurements. In most TDMA studies, a residence time in the order of seconds is used for humidification (or dehumidification). NaCl and $(NH_4)_2SO_4$ particles are usually used to verify the equilibrium measurements during this residence time, which is presumed to be sufficient for other particles. There have been observations that not all types of submicrometer particles, including atmospheric particles, attain their equilibrium sizes within this time scale. We recommend that experimentation with different residence times be conducted and that the residence time should be explicitly stated in future TDMA measurements. Mass transfer effects may also exist in the measurements of other properties related to the water uptake of atmospheric particles such as relative humidity dependent light scattering coefficients and cloud condensation nuclei activity.

1 Introduction

Atmospheric particles play an important role in the global climate change and in the chemistry of the troposphere. Determining the phase (solid or liquid) and size of atmospheric particles at different relative humidities (RH) and temperatures is important for elucidating the role of atmospheric particles in many atmospheric processes such as the absorption and scattering of solar radiation (Martin et al., 2004), heterogeneous reactions between gas molecules and particles (Hu and Abbatt, 1997), and cloud condensation nuclei (CCN) activity (Bilde and Svenningsson, 2004; Hartz et al., 2005[1]).

The hygroscopicity of aerosol particles is commonly reported in terms of particle size (or mass) changes as a function of RH under saturation conditions. The aerosol water content is obtained by comparing the wet and dry particle sizes (or masses). When deliquescence (solid to liquid) or crystallization (liquid to solid) phase transitions occur, a spontaneous sharp change in particle size arises. Hygroscopicity data are useful in parameterizing thermodynamic models (Chan et al., 1997; Clegg et al., 1997, 2003; Ming and Russell, 2003; Topping et al., 2004) and revealing the state of the mixing of atmospheric particles (Cocker et al., 2001a). They are also needed for modeling the physicochemical properties of atmospheric particles, including their roles in global radiative forcing (Martin, 2000) and CCN activity (Rissler et al., 2004; Kreidenweis et al., 2005).

Most hygroscopicity measurements of aerosols, especially in field studies, are made with a tandem differential mobility analyzer (TDMA), also called Hygroscopic TDMA by some researchers (Liu et al., 1978; Rader and McMurry, 1986; McMurry and Stolzenburg, 1989; Swietlicki et al., 1999; Cruz and Pandis, 2000; Dick et al., 2000; Gysel et al., 2004). A key issue in investigating the hygroscopicity of the particles is if the particles have attained their equilibrium state in the measurements. In this paper, we conduct a survey in the literature on TDMA measurements (see Tables 1 and 2) and present evidence that hygroscopicity measurements can be potentially compromised by mass transfer effects attributed to the insufficient time allowed for particle growth or evaporation. We recommend that the residence time for humidification or dehumidification in TDMA studies be explicitly reported and that equilibrium measurements be confirmed.

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Table 1. Summary of Hygroscopic Measurement of Laboratory Generated Particles Utilizing the TDMA.

Study	Chemical species studied	Residence time (s)[a]	Initial particle size (nm)[b]	Growth or evaporation (Range of RH studied)
Organic compounds or mixtures of an inorganic salt and an organic compound				
Brooks et al. (2004)	Fluka fulvic acid (FA), Pahokee peat reference humic acid (HA), Leonardite standard HA, Suwannee river reference FA, Phthalic acid, Polyacrylic acid, Their mixtures with $(NH_4)_2SO_4$		50, 100, 200	Growth (15–95%RH)
Gysel et al. (2004)	Water soluble matters and humic-like substances isolated from PM1.5 aerosol samples, Nordic reference fulvic and humic acids	8	103	Growth and Evaporation (5–90%RH)
Johnson et al. (2004)	Di-2-ethylhexyl-sebacate (DEHS), Methanesulphonic acid (MSA), $(NH_4)_2SO_4$ – MSA, NaCl seeded DEHS	13.4	100	Growth (90%RH)
Mikhailov et al. (2004)	Protein bovine serum albumin (BSA), NaCl-BSA, $(NH_4)NO_3$–BSA	7.5–18.5	100–201	Growth and Evaporation (<5–95%RH)
Mochida and Kawamura, (2004)	Levoglucosan, D-Glucose, Vanillic, Syringic, 4-hydroxybenozoic acids		100	Growth (5–95%RH)
Sjogren et al. (2004)	Adipic acid, $(NH_4)_2SO_4$ – adipic acid	1–120		Growth (10–90%RH)
Prenni et al. (2003)	$(NH_4)_2SO_4$ – oxalic acid, $(NH_4)_2SO_4$ – malonic acid, $(NH_4)_2SO_4$ – succinic acid, $(NH_4)_2SO_4$ – glutaric acid, $(NH_4)_2SO_4$ – adipic acid		100	Growth (30–95%RH)
Hameri et al. (2002)	Adipic acid, Phthalic acid, $(NH_4)_2SO_4$-adipic acid, $(NH_4)_2SO_4$-phthalic acid, $(NH_4)_2SO_4$-succinic acid, $(NH_4)_2SO_4$-malonic acid	4.4	100	Growth (50–90%RH)
Prenni et al. (2001)	Oxalic acid, Malonic acid, Succinic acid, Glutaric acid, Adipic acid		50, 100	Growth (45–95%RH)
Cruz and Pandis (2000)	Glutaric acid, Pinonic acid, NaCl-glutaric acid, $(NH_4)_2SO_4$-glutaric acid, NaCl-pinonic acid, $(NH_4)_2SO_4$-pinonic acid	30	50, 80, 100	Growth (35–95%RH)
Chen and Lee (1999)	Sodium oleate, Tween 80, Span80, Sodium dedecyl sulfate (SDS), CaCl- Sodium oleate, CaCl-Tween 80, CaCl-Span80, CaCl –SDS	15	74	Growth (7–85%RH)
Inorganic Salt and Mixtures of Inorganic salts				
Johnson et al. (2004)	NaCl, $(NH_4)_2SO_4$, $NaNO_3$, NH_4HSO_4, H_2SO_4	13.4	100	Growth (90%RH)
Mikhailov et al. (2004)	NaCl, $(NH_4)NO_3$	7.5–18.5	100–201	Growth and Evaporation (<5–95%RH)
Sjogren et al. (2004)	$(NH_4)_2SO_4$	1–120		Growth (10–90%RH)
Pagels et al. (2003)	K_2SO_4, K_2CO_3		100	Growth (25–90%RH)
Gysel et al. (2002)	NaCl, $(NH_4)_2SO_4$, $NaNO_3$	60	100	Growth and Evaporation (5–95%RH)
Hameri et al. (2001a)	NaCl		8–50	Growth and Evaporation (<5–90%RH)
Brechtel and Kreidenweis (2000)	NaCl, $(NH_4)_2SO_4$, NH_4HSO_4, NaCl-$(NH_4)_2SO_4$		25–102	
Cruz and Pandis (2000)	NaCl, $(NH_4)_2SO_4$	30	50, 80, 100	Growth (35–95%RH)
Hameri et al. (2000)	$(NH_4)_2SO_4$		8–50	Growth and Evaporation (<5%–90 RH)
Hansson et al. (1998)	NaCl	10–20	50, 100, 200	Growth and Evaporation (30–90%RH)
Ristovski et al. (1998)	NaCl	2.2–7.4	50	Growth (50–∼100%RH)
Xiong et al. (1998)	H_2SO_4	6–10	40–120	Growth (20–85%RH)
Soot Particles				
Gysel et al. (2003)	Source: Jet engine combustor		30, 50, 100	Growth (70–90%RH)
Pagels et al. (2003)	Source: Moving gate boiler		35–350	Growth (25–90%RH)
Dua et al. (1999)	Source: Resident wood stove		30–250	Growth (>99%RH)
Weingartner et al. (1997)	Source: Diesel engines	2.2–10	51.5, 73, 108	Growth (>99%RH)
Smokes particles				
Dua and Hopke (1996)	Source: different kind of oil during deep frying, sausages during grilling, burning wood in a stoves		50–325	Growth (∼100%RH)
Organic Coating				
Hansson et al. (1998)	NaCl coated with tetracosane acid, octanoic acid, lauric acid	10–20	50, 100, 200	Growth and Evaporation (30–85 RH)
Xiong et al. (1998)	H_2SO_4 coated with lauric acid, stearic acid, oleic acid	6–10	40–120	Growth (20–85%RH)
Secondary Organic Aerosols (SOA)				
Saathoff et al. (2003)	SOA formed from ozonolysis of α-pinene (Diesel soot, $(NH_4)_2SO_4$ as seed particles)		100, 200	Growth and Evaporation (15–90%RH)
Cocker et al. (2001b)	SOA formed from ozonolysis of α-pinene ($CaCl_2$, $(NH_4)_2SO_4$, $(NH_4)HSO_4$ as seed particles)	10	136, 235	Growth (5–89%RH)
Cocker et al. (2001c)	SOA formed from ozonolysis of m-xylene and 1,3,5-trimethylbenzene ($(NH_4)HSO_4$ as seed particles)	10 refer to Cocker et al. (2001b)	136, 235	Growth (85%RH)
Virkkula et al. (1999)	SOA formed from oxidation of α-pinene, β−pinene, and limonene ($(NH_4)_2SO_4$ as seed particles)	2.4	30–200	Growth (81–87%RH)

[a] The residence time of the submicrometer particles in a RH conditioner (humidifier or dehumidifier). [b] Particle size selected by the first DMA.

Table 2. Summary of Hygroscopic Measurement of Atmospheric Particles Utilizing the TDMA.

Study	Sampling Period and Location	Residence Time (s)^{a}	Chemical Species ^{b}	Initial Particle Size (nm)^{c} (RH in the dryer)	Growth or Evaporation (Range of RH Studied)
Carrico et al. (2005)	July–September, 2002, Yosemite National Park, California, U.S.	∼2.5	$(NH_4)_2SO_4$	100, 200 (drying RH: <5%RH)	Growth (40–90%RH)
Ferron et al. (2005)	Winter, summer and fall, 1998, Bavaria, Germany		NaCl	50, 100, 150, 250	Growth (85%RH)
Santarpia et al. (2005)	August and September, 2002, Texas, U.S.		NaCl	12–400 (drying RH: 20%RH)	Growth and Evaporation (30–85%RH)
Aklilu and Mozurkewich (2004)	August, 2001, British Columbia, Canada		$(NH_4)_2SO_4$	50, 80, 114, 160 (drying RH: 15%RH)	Growth (50–85%RH)
Gasparini et al. (2004)	June–October, 2001, Texas, U.S.		NaCl	25–344 (drying RH: 20%RH)	Growth (84%RH)
Rissler et al. (2004)	July, 2001, Balbina, Amazonia, Brazil		$(NH_4)_2SO_4$	20–265 (drying RH: RH<10%)	Growth (90%RH)
Santarpia et al. (2004)	August, 2002, Texas, U.S.		NaCl	160, 320 (drying RH: 20%RH)	Growth and Evaporation (30–85%RH)
Chen et al. (2003)	October–December, 2001, Taipei, Taiwan	6	NaCl, $(NH_4)_2SO_4$	53, 82, 95, 202 (drying RH: <20%RH)	Growth (60–90%RH)
Massling et al. (2003)	January–February, 1999, Atlantic Ocean and February–March, 1999, Indian Ocean		NaCl, $(NH_4)_2SO_4$ KCl	50, 150, 250 (drying RH: <5%RH)	Growth (30, 55, 75, 90%RH)
Nessler et al. (2003)	February–March, 2000, Jungfraujoch, Switzerland	60 refer to Weingartner et al. (2002)		50, 100, 250 (drying RH: ∼10%RH)	Growth (10–85%RH)
Baltensperger et al. (2002)	May–June, 1998, Bresso, Milan, Italy	60 refer to Weingartner et al. (2002)		50–200 (drying RH: <30%RH)	Growth (90%RH)
Busch et al. (2002)	July–August, Falkenberg, Berlin, Germany		NaCl	50, 100, 150, 250	Growth (60 and 90%RH)
Buzorius et al. (2002)	Cheju Island, Republic of South Korea		$(NH_4)_2SO_4$	250	Growth (>90%RH)
Roberts et al. (2002)	March–April, 1998, Amazonia, Brazil		NaCl, $(NH_4)_2SO_4$	35–264 (drying RH: <10%RH)	Growth (70 and 90%RH)
Vakeva et al. (2002a)	1997–1999, Helsinki, Luukki, Hyytiala, Finland and Western Ireland		$(NH_4)_2SO_4$	10, 20	Growth (90%RH)
Vakeva et al. (2002b)	September, 1998, and June, 1999, west coast of Ireland		$(NH_4)_2SO_4$	8–20	Growth (90%RH)
Weingartner et al. (2002)	March, 2000, Jungfraujoch, Switzerland	60	$(NH_4)_2SO_4$	50, 100, 250 (drying RH: <15%RH)	Growth (10–85%RH)
Zhou et al. (2002)	March–April, 1998, Amazonia, Brazil		NaCl, $(NH_4)_2SO_4$	35–264 (drying RH: <5%RH)	Growth (90%RH)
Cocker et al. (2001a)	August–September, 1999, Pasadena, California, U.S.			50, 150 (drying RH<10%RH)	Growth (89%RH)
Hameri et al. (2001b)	Hyytiala forest, Finland	0.1 (residence time in RH conditioner)	$(NH_4)_2SO_4$	20–365 (drying RH: <5%RH)	Growth (90%RH)
Zhou et al. (2001)	July–August, 1996, Arctic Ocean		NaCl	15, 35, 50, 165 (drying RH: <10%RH)	Growth (50, 70, 90%RH)
Dick et al. (2000)	July–August, 1995, Great Smoky Mountain National Park, U.S.	1.3–5.0		50, 100, 200, 300, 400 (drying RH: ∼5%RH)	Growth (5–85%RH)
Swietlicki et al. (2000)	June–July, 1997, 5 sites in the subtropical North Eastern Atlantic	1–2	NaCl, $(NH_4)_2SO_4$	35-440 (drying RH: <10%RH)	Growth (<10%–90%RH)
Swietlicki et al. (1999)	March–April, 1995, Great Dun Fell, England		NaCl	35–265 (drying RH: <10%RH)	Growth (90%RH)
Berg et al. (1998)	October–November, 1995, Pacific Ocean November–December, 1995, Southern Ocean		NaCl, $(NH_4)_2SO_4$	35–165 (DMA1: <10%RH)	Growth (89 or 90%RH) Evaporation (50, 60%RH)
Covert et al. (1998)	November and December, 1995, Cape Grim, Tasmania			30, 50, 150, 250 (drying RH: ∼25%RH)	Growth (90%RH)
Svenningsson et al. (1997)	April and May, 1993, Great Dun Fell, England		NaCl, $(NH_4)_2SO_4$	50, 75, 110, 165, 265 (drying RH: <20%RH)	Growth (90%RH)
McMurry et al. (1996)	September, 1994, Minneapolis, U.S.			300–400 (drying RH: 48%RH)	Growth (87%RH)
Saxena et al. (1995)	Grand Canyon and Los Angeles, U.S.	1.3–5.0 refer to McMurry and Stolzenburg (1989)	NaCl, H_2SO_4, $(NH_4)_2SO_4$	16–500 (drying RH: ambient RH)	Growth (80–93%RH)
Pitchford and McMurry (1994)	January–March, 1990, Grand Canyon National Park, Arizona, U.S.			15–400	Growth (3–90%RH)
Svenningsson et al. (1994)	October and November, 1990, Kleiner Feldberg, Taunus, Germany			50, 150, 300 (DMA1: ∼10–20% RH)	Growth (<20–85%RH)
Covert and Heintzenberg (1993)	March and April, 1989, Ny Alesund, Svalbard		$(NH_4)_2SO_4$	110, 200, 310 (DMA1: 20% RH)	Growth (90%RH)
Zhang et al. (1993)	1987 and 1990, Claremont, Los Angeles and Grand Canyon, U.S.	1.3-5.0 refer to McMurry and Stolzenburg (1989)	NaCl, H_2SO_4, $(NH_4)_2SO_4$	15–400 (drying RH: ambient RH)	Growth (3–90%RH)
Svenningsson et al. (1992)	November, 1989 Po Valley, Italy		NaCl, $(NH_4)_2SO_4$	30, 50, 100, 150, 200	Growth (85%RH)
McMurry and Stolzenburg (1989)	June and September, 1987, Claremont, Los Angeles, U.S.	1.3–5.0	NaCl, H_2SO_4, $(NH_4)_2SO_4$	50, 200, 500 (drying RH: ambient RH)	Growth (7–90%RH)

[a] The residence time of the submicrometer particles in a RH conditioner (humidifier or dehumidifier). [b] Chemical species used to check the performance of the TDMA system. [c] Particle size selected by the first DMA. It is noted that atmospheric aerosols are dried in the first DMA instead of diffusion dryer in some studies. The drying RH is the RH inside the dryer unless specified otherwise.

2 Measurement techniques

TDMA and the electrodynamic balance (EDB) (Richardson and Spann, 1984; Cohen et al., 1987; Ray et al., 1989; Chan et al., 1992; Tang and Munkelwitz, 1993, 1994; Chan and Chan, 2003) are the most commonly used techniques for hygroscopicity measurements and their measurements are often compared. Comprehensive summaries of previous laboratory studies have been presented by Martin (2000) and Kanakidou et al. (2005). A summary of laboratory TDMA studies has been presented in Table 1. Other techniques include single particle mass spectrometry (Ge et al., 1996, 1998), ambient-dry aerosol size spectrometer (Stanier et al., 2004), RH-controlled nephelometry (ten Brink et al., 2000), aerosol cell–microscope system (Pant et al., 2004; Parsons et al., 2004), aerosol flow tube–Fourier Transform Infrared (FTIR) system (Brooks et al., 2003; Braban and Abbatt, 2004), RH-controlled optical particle counter (Ames et al., 2000; Hand et al., 2000; Kreisberg et al., 2001), filter-based analysis by beta attenuation (or gravitational method) (Hitzenberger et al., 1997; Speer et al., 1997), and water activity measurements of bulk aqueous solutions (Brooks et al., 2002; Wise et al., 2003; Marcolli et al., 2004).

We focus our discussions on TDMA measurements in this paper. A typical TDMA system consists of a diffusion dryer, two differential mobility analyzers (DMA), an RH conditioner (humidifier or dehumidifier) set between the two DMA, and a condensation particle counter (CPC). Initially, atmospheric (or laboratory-generated) polydispersed particles are dried in a diffusion dryer. Monodispersed particles (a few to hundreds of nanometers in mobility diameter) selected by a DMA are then passed through the RH conditioner, in which humidification of the particles takes place. The size of the particles leaving the RH conditioner is measured with the other DMA and the CPC (Rader and McMurry, 1986; McMurry and Stolzenburg, 1989). Different configurations of TDMA systems have been employed in atmospheric aerosol studies (Chuang, 2003; Santarpia et al., 2004). The TDMA reports the relative change in the particle mobility diameter or the growth factor, G_f, which is the ratio of the particle diameter at a high RH to a dry particle diameter at reference RH, as a function of RH.

An EDB utilizes a combination of an alternating current electric field and a direct current electric field to levitate single particles (Davis, 1997). A charged particle can be levitated and kept stationary when the electrostatic force it experiences balances its weight. Hence, relative mass measurements due to humidity changes can be made by adjusting the DC voltage required to make the particle stationary. In hygroscopicity measurements, the measurements of a particle under multiple stepwise increases (or decreases) in RH and the mass of the particle is determined as a function of RH. Data in terms of the mass ratio or the mass fraction of the solute are reported at different RH. The data can be converted to G_f (or vice versa) with the determination of the particle density for comparison with the TDMA measurements. In contrast to the TDMA, the EDB measures the hygroscopicity of the particles that are few to tens of μm in diameter and it can only measure laboratory-generated particles.

3 Equilibrium measurement

Theoretical analysis of the gas-particle equilibrium time scales for the water uptake for a non-volatile particle is available in the literature (Kerminen, 1997). In gas condensation, the flux of a species into a single particle, I_i, can be described by:

$$I_i\left(d_p\right) = \frac{2\pi D_i [C_i - C_{i,eq}\left(d_p\right)]}{1 + 2\lambda/\alpha_i d_p} \qquad (1)$$

where d_p is the particle diameter, D_i is the gas-phase diffusion coefficient of the species, i, C_i and $C_{i,eq}$ are its concentration in the gas phase and over the particle surface, respectively, λ is the air mean free path, and α is the accommodation coefficient accounting for the imperfect accommodation of the species on the particle surface. Kerminen (1997) estimated the time required for the achievement of water equilibrium to be between 8×10^{-6}s and 0.1 s for 100 nm and 500 nm particles at 90%RH and at 0°C and 25°C with different accommodation coefficients (0.001 to 1). The typical residence time of a few seconds in the RH conditioner in TDMA measurements is adequate for most equilibrium hygroscopic measurements. Significantly longer equilibrium time may be required when the accommodation coefficient is much less than 0.001. Chuang (2003) found that some atmospheric particles exhibited equilibrium time scale in the order of seconds to tens of seconds in their TDMA measurements. He estimated that the accommodation coefficients of these particles are in the range of 10^{-4} to 10^{-5}. This falls into the lower range of values reported in laboratory experiments using model aerosols with single component films. Atmospheric particles containing organic films resulting in an accommodation coefficient in the range of 10^{-4} to 10^{-5} may not achieve equilibrium in TDMA experiments.

Most researchers choose NaCl or $(NH_4)_2SO_4$ particles to verify the time scale for equilibrium measurements with the implicit assumption that the water vapor-particle equilibrium is also achieved for other particles, including atmospheric particles, in the same time scale (order of seconds). However, in addition to possibility of having particles of a very low accommodation coefficient, transport effects in very viscous particles can also hinder gas-particle equilibrium (Seinfeld, 1986; Kerminen, 1997; Chan et al., 1998). Chan and coworkers have experimentally shown that the achievement of equilibrium of some aqueous droplets can be hindered by the transport limitation inside the droplets in their EDB measurements. For example, Chan et al. (2000) found that there is a significant retardation of water evaporation (and growth) rate of magnesium sulfate ($MgSO_4$) droplets at high concentrations (at low RH). Using Raman spectroscopy, Zhang and Chan (2000) attributed this delay to the formation of contact ion pairs and chain structures in highly concentrated droplets of $MgSO_4$. Moreover, Peng et al. (2001) observed that glutaric acid particles took a significant longer time (∼10 h) to completely deliquesce, compared to other dicarboxylic acids and multifunctional acids particles (∼40 min). This mass transfer limitation in the growth process was also observed in sodium pyruvate particles by Peng and Chan (2001). These significant retardations in growth or evaporation rates were not found for NaCl or $(NH_4)_2SO_4$ particles in their EDB measurements. Overall, mass transfer effects in hygroscopic measurements of ambient particles and laboratory generated particles are possible if the particles are not allowed to have sufficient time to achieve their equilibrium sizes in the RH conditioner. Residence time of a few seconds may not be adequate, depending on the nature of the particles.

4 Mass transfer effects in the TDMA measurements

4.1 Laboratory measurements

A number of hygroscopicity measurements of inorganic salt particles (e.g., NaCl, $(NH_4)_2SO_4$, and NH_4NO_3) using TDMA and EDB have been reported. There is a general agreement on the hygroscopicity of typical inorganic salt particles although some discrepancies between the data have been observed. For example, different crystallization characteristics of some supersaturated droplets (e.g., NH_4NO_3) have been attributed to the presence of impurities that may have heterogeneously seeded the crystallization (Martin, 2000).

The hygroscopicity of glutaric acid particles as a function of RH has been measured by Cruz and Pandis (2000) and Prenni et al. (2001) using TDMA and by Peng et al. (2001) using EDB. Cruz and Pandis (2000) reported a G_f of approximately 1.10 at 90%RH. On the other hand, Prenni et al. (2001) reported a G_f of 1.29, which is close to a G_f of 1.30 reported by Peng et al. (2001). Solute evaporation loss in semi-volatile glutaric acid particles, the Kelvin effect, and the shape factor in converting the mobility diameter to the geometric diameter do not account for the differences in the G_f. The results of Peng et al. (2001) and Prenni et al. (2001) were consistent with those inferred from the water activity measurements of aqueous glutaric acid solution after deliquescence, suggesting that the glutaric acid particles had reached their equilibrium sizes.

Furthermore, Peng et al. (2001) observed that glutaric acid particles continued to absorb water for several hours during deliquescence at 83–85%RH, which was much longer than the approximately 40 min required for other dicarboxylic acid particles (e.g., malonic acid) to reach their equilibrium sizes in their EDB measurements (the rather long equilibration time in EDB measurements is because of the time required to change the RH inside the EDB). This observation suggested that glutaric acid particles exhibited a strong kinetic effect during deliquescence and required a longer equilibrium time than did inorganic salt and the other dicarboxylic acid particles they studied. Although Cruz and Pandis (2000) reported that NaCl and $(NH_4)_2SO_4$ particles attained their equilibrium sizes with residence times longer than 10 s, the residence time of the glutaric acid particles was not tested. Peng et al. (2001) attributed the lower G_f of glutaric acid particles reported by Cruz and Pandis (2000) after deliquescence to the mass transfer effects in the TDMA growth measurements. These observations suggest that the time required for NaCl and $(NH_4)_2SO_4$ particles to achieve their equilibrium sizes may not necessarily be sufficient for particles of other chemical systems, including possibly atmospheric particles.

Various studies have reported the dependence of G_f of the particles on the residence time. Ristovski et al. (1998) observed that the G_f of NaCl particles increased from approximately 1.1 to 1.9 at 90%RH when the residence time increased from 2.2s to 7.4s. Cruz and Pandis (2000) reported that the G_f of NaCl and $(NH_4)_2SO_4$ particles after humidification were independent of the residence time only when the residence time was longer than 10s but not shorter. Sjogren et al. (2004) found that $(NH_4)_2SO_4$-adipic acid particles (50 wt% and 76wt% adipic acid) exhibited a lower G_f at a residence time of less than 4 s than the G_f at more than 4 s at 78–91%RH after deliquescence.

Xiong et al. (1998) found that submicrometer sulfuric acid (H_2SO_4) particles attained their equilibrium size within 6 s. On the other hand, the G_f of H_2SO_4 particles coated with three monolayers of lauric acid further increased as the residence time increased from 6 s to 10 s, providing evidence that the coated H_2SO_4 particles had not yet reached their equilibrium size within 6 s. Organic films can act a physical barrier to retard the water condensation (or evaporation) rate in planar solutions and on particle surfaces (Gill et al., 1983; Barnes, 1986) and can lower the accommodation coefficient (Pandis et al., 1995). A summary of laboratory studies on the evaporation and condensation rates of water vapor from particles in the presence of organic films has been presented by Chuang (2003).

4.2 Field measurements

Unlike for laboratory-generated particles, the chemical compositions of atmospheric particles are generally unknown a priori and comparison of measurements with literature data on the identified chemical systems is not practical. Previous studies on the hygroscopicity of atmosphere particles using TDMA have been summarized by Cocker et al. (2001a) and Kanakidou et al. (2005). These studies and more recent field studies are summarized in Table 2. The performance of the TDMA is usually checked by measuring the hygroscopicity of NaCl and $(NH_4)_2SO_4$ particles, whose hygroscopic properties (G_f , deliquescence RH, crystallization RH) are well known. As can be seen in Table 2, the residence time of submicrometer atmospheric particles in the RH conditioner is usually not explicitly stated in the studies. The reported values are usually on the order of a few seconds (<6 s), which is often presumed to be sufficient to capture the hygroscopicity of atmospheric particles.

Chuang (2003) conducted an experiment in which atmospheric particles were humidified in two tandem humidifiers (instead of one in conventional TDMA measurements) to determine the equilibrium time scale of water uptake for atmospheric particles. He reported that most atmospheric particles reached their equilibrium sizes in less than 2 s to 3 s at ∼90%RH during both the dry and wet seasons in Mexico City. On the other hand, a small number of atmospheric particles (0 to 2% depending on particle size and season) exhibited equilibrium time scales longer than 3s but less than approximately 33 s. He found that these atmospheric particles with diameters of 50 nm and 100 nm leaving the first humidifier further grew to 59–97.7 nm and 122–181 nm at ∼90%RH, respectively, after further humidification in the second humidifier. Such results suggest that the assumption of reaching equilibrium within 2–3 s in the first humidifier may substantially underestimate the water content and size of some atmospheric particles.

Chuang (2003) also postulated that these atmospheric particles exhibiting longer equilibrium times have an approximate accommodation coefficient in the range of 1×10^{-5} to 4×10^{-5} and may have a coating of organic film. Although the portion of atmospheric particles requiring longer equilibrium times in the TDMA is small in Chuang's study, organic films have been commonly found on atmospheric particles (Gill et al., 1983; Pofasi et al., 1998, 2003; Russell et al., 2002; Tervahattu et al., 2002ab; Li et al., 2003). To date, field TDMA studies have assumed that a few seconds is long enough residence time for atmospheric particles, including particles with organic coatings and water-inhibiting substances, to achieve their equilibrium size (Swietlicki et al., 2000). McMurry and Stolzenburg (1989) pointed out that the effects of organic coatings or surfactants in atmospheric particles on the equilibrium time are unknown. It is possible that an organic coating or surface-active compounds can hinder the transport of water across the particle/air interface and result in non-equilibrium growth measurements in field studies using a TDMA (Xiong et al., 1998).

5 Conclusions

This paper considers the issue that, due to the short residence time allowed to bring particles to equilibrium, there is a possibility of mass transfer effects complicating equilibrium hygroscopicity measurements in a TDMA in field and laboratory measurements. The equilibrium time of a few seconds is adequate for equilibrium particle growth/evaporation in typical inorganic salt particles such as NaCl and $(NH_4)_2SO_4$, but it may not be adequate for other particles such as those coated with organic layers. Chan and coworkers have found significant mass transfer effects in EDB hygroscopicity measurements for some inorganic salt particles such as $MgSO_4$ (Ha and Chan, 1999; Zhang and Chan, 2000) and organic particles such as sodium pyruvate, arginine, and asparagine (Peng and Chan, 2001; Chan et al., 2005). Although particles studied in the EDB are 2 orders of magnitude larger and would take a longer equilibration time than those studied in the TDMA, these results suggest the possibility that longer equilibrium time scales may be required for TDMA measurements of these single or multicomponent particles, as discussed for glutaric acid particles earlier. Equilibrium measurements of other chemical systems with the selected residence time in TDMA measurement can be assessed by comparing the results from known studies or bulk water activity data at high RH if available.

Mass transfer effects may also complicate measurements in other types of aerosol flow-through systems that have residence times on the order of seconds for humidification or dehumidification (e.g., RH controlled nephelometry, ambient-dry aerosol size spectrometer, and aerosol flow tube–FTIR system) and for the activation of particles to form clouds under supersaturated conditions. We recommend that, in addition to reporting the particle size chosen for growth studies, the residence time should also be explicitly reported and that measurements in a range of residence times be tested.

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