Equilibrium times for hygroscopic growth of submicrometer aerosol

S. Sjögren, E. Weingartner, U. Baltensperger
Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, CH-5232 Villigen, Switzerland

Aerosol particles influence the radiation balance of the Earth, and thus the climate, with the direct and indirect aerosol effect. The hygroscopicity of the aerosol plays a role for these phenomena. To quantify the hygroscopicity an H-TDMA (Hygroscopicity Tandem Differential Mobility Analyser, Weingartner *et al*., 2002) is most commonly employed. Here is shown how mass transfer of water into aerosols can take a rather long time (several seconds), also for particles with a diameter as small as 100 to 300 nm. This is the case especially for mixtures of organic/inorganic substances, such as carboxylic acids mixed with ammonium sulphate. Such particle compositions are more representative for atmospheric aerosols, as have been measured at the Jungfraujoch high alpine research station, a European air background site. Aerosols generated from pure inorganic salts have substantially faster equilibrium times.

The mass transfer of water vapour to the surface of a particle is in general not considered to be the limiting step to reach gas-particle equilibrium (condensation theory, as shown by Kerminen, 1997). However, water transport limitations inside the particle may occur, on a time-scale comparable to the residence times used in H-TDMA instruments. Laboratory measurements were made with different residence times (1 s. to 2 min.) at the studied RH, to determine the equilibrium time for different mixtures. As the number of components increased and especially as slightly hydrophilic substances were studied (humic acid), the equilibrium time increased to as long as 30 s.

It is thus important that the H-TDMA instruments used for measurement campaigns have a sufficient residence time at the studied RH in order to report a correct hygroscopic growth. The determination of the equilibrium time for typical atmospheric particles and sizes are necessary as next step.

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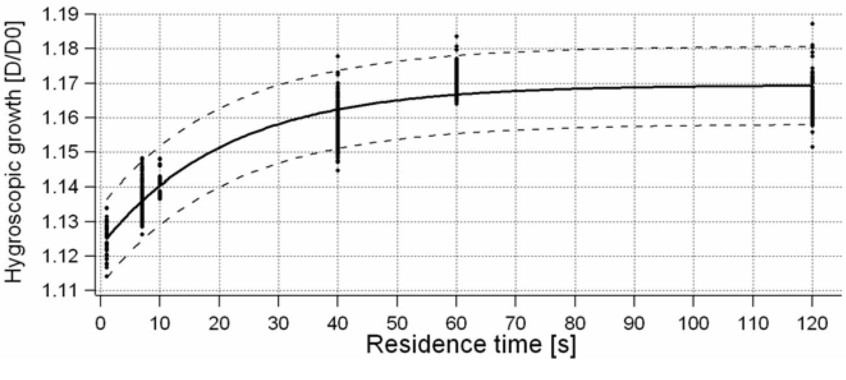


Fig. 1 Change in growth factor of ammonium sulphate-humic acid mixture (23/77 % by mass) measured for different residence times (90 %RH). Up to 20 s. or more are needed for a measurement at equilibrium.

EQUILIBRIUM TIME FOR HYGROSCOPIC GROWTH OF SUBMICROMETER AEROSOL MIXTURES

S. Sjögren[1], E. Weingartner[1], U. Baltensperger[1]
M. Cubison[2], H. Coe[2]
1) Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland
2) UMIST, P.O. Box 88, Manchester M60 1QD, UK

INTRODUCTION

Figure 1. Direct effect of aerosols – reflection or absorption of radiation. Indirect effect – influencing cloud albedo.

Aerosol particles influence the radiation balance of the Earth, and thus the climate, with the direct and indirect aerosol effect. The hygroscopicity of the aerosol plays a role for these phenomena. In the past, the first climate models used ammonium sulphate, a common component of the atmospheric aerosol, as model substance. It has since shown that the aerosol generally consists of a range of substances (Choi *et al*., 2002). The hygroscopic properties of mixtures are now studied and will be incorporated into climate models.

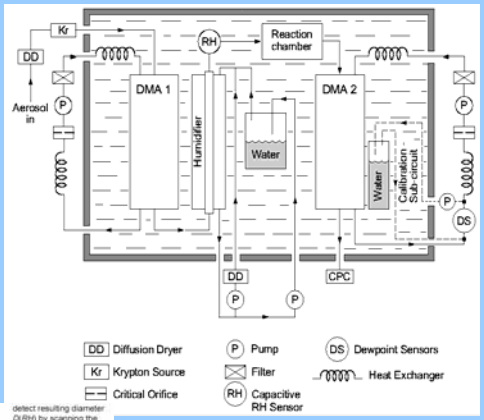
To quantify the hygroscopicity of particles an H-TDMA (Hygroscopicity Tandem Differential Mobility Analyser, Rader *et al*., 1986, Weingartner *et al*., 2002) is commonly employed.

This poster shows the hygroscopicity measured for some mixtures not reported before, and especially the water vapour equilibrium time needed for such H-TDMA measurements.

EXPERIMENTAL SETUP

Two H-TDMA instruments (PSI and UMIST) were employed. They functioned in a similar manner. A first DMA1 selected at dry conditions a monodisperse aerosol size, D0. The aerosol passed through a humidifier with a controlled relative humidity RH, and the changed diameter D was measured with a second DMA2. The humidity was continuously changed from ~10 to 90% RH during about two hours. The measured growth factor g is defined as D/D0.

In order to study the effect of residence time of the aerosol, chambers of different volumes were installed after the humidifier (before entry to DMA2), allowing the aerosol to equilibrate at the specified RH for a range of residence times.



DD	Diffusion Dryer	P	Pump	DS	Dewpoint Sensors
Kr	Krypton Source	☒	Filter	―ꝏꝏ―	Heat Exchanger
――	Critical Orifice	RH	Capacitive RH Sensor		

Figure 2. Experimental setup H-TDMA.

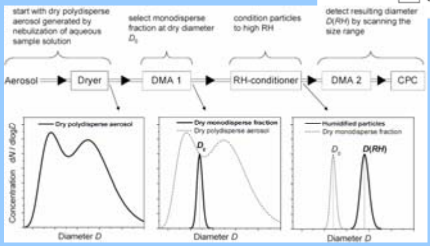


Figure 3. H-TDMA instrument to measure hygroscopic growth factors g = D(RH)/D0 of aerosol particles. Abbreviations are: DMA for differential mobility analyzer and CPC for condensation particle counter.

RESULTS AND DISCUSSION

An intercomparison was made between two H-TDMA instruments, measuring the hygroscopicity of ammonium sulphate (AS) and mixtures of AS, adipic acid (AA) and humic acid (HA). The intercomparison was a good opportunity to compare two different instruments. The results showed good correspondence with literature and theory (Figure 4).

To investigate the equilibrium times for some different aerosol mixtures of ammonium sulphate and organic substances the response to a change in relative humidity (RH) was measured with varying time. It is shown that mass transfer of water into aerosols can take a rather long time (several seconds), also for submicrometer particles (Figure 6 and 7). This is the case especially for mixtures of organic/inorganic substances, such as carboxylic acids mixed with ammonium sulphate. Carboxylic acids have been analysed as a large constituent of the organic fraction of atmospheric aerosol. It is tempting to assume that a larger fraction of adipic acid causes a longer equilibrium time (figure 6). It is also interesting to note the decreased deliquescence RH with increasing adipic acid content, which has been proposed (Seinfeld, 1998).

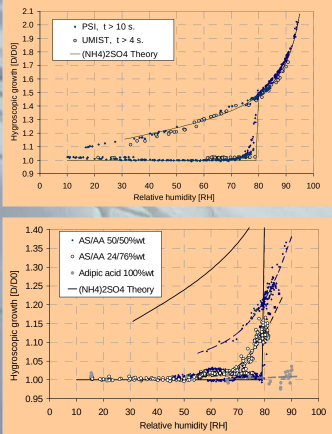


Figure 4. Humidogram of ammonium sulphate (top) and mixtures AS and adipic acid (bottom). Diameter 100 nm.

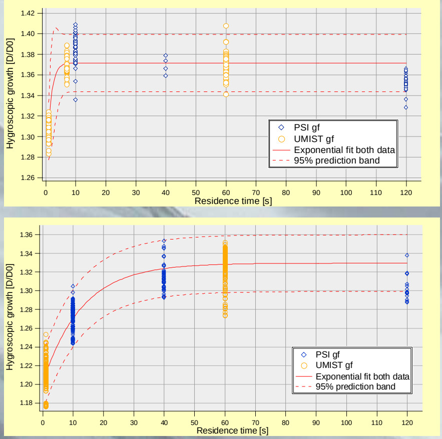


Figure 6. Hygroscopic growth measured with different residence times. Ammonium sulphate-adipic acid mixture, 50/50%wt (top) and 24/76%wt (bottom). 90 %RH, diameter 100 nm.

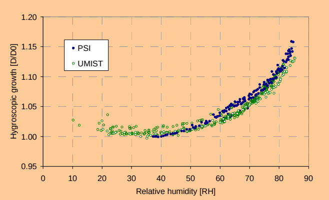


Figure 5. Humidogram of mixtures of AS and humic acid acid (23/77%wt). Diameter 140 nm.

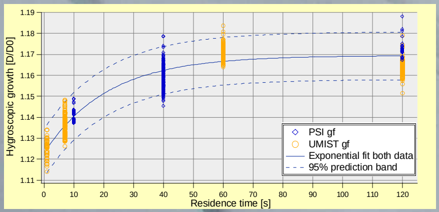


Figure 7. Hygroscopic growth measured with different residence times. Ammonium sulphate-humic acid mixture (23/77%wt). 90 %RH, diameter 140 nm.

Aerosols generated from pure inorganic salts have substantially faster equilibrium times, although mixtures of several salts (sea-side aerosol for example) might have some mass transfer limitations as well.

As model substance for the water soluble organic content (WSOC) humic acids are sometimes used. The equilibrium time for a 23/77%wt AS/HA mixture is also in the order of seconds (Figure 7).

Thus it is important to allow sufficient residence time at the set humidity to allow the aerosol to reach equilibrium in the H-TDMA. A to short residence time would result in a to low growth factor measured.

It has been shown that different fractions of atmospheric urban aerosol require different equilibrium times for hygroscopic growth (Chuang, 2003). Small fractions exist which have longer equilibrium times. Thus, to examine how a certain aerosol responds to humidity could improve results, for example before a longer measurement campaign.

Comparison growth factor	This study	Prenni et al. (2003)	Hameri et al. (2002)
AS/AA 50/50%wt at 80%RH	1.21	1.20	1.24
AS/AA 50/50%wt at 90%RH	1.37	1.35	-

Figure 8. Comparison of growth factor with literature values.

CONCLUSION AND PERSPECTIVE

It is shown that for simple organic-inorganic systems, a residence time of a few seconds at high humidity is required for hygroscopic growth (condensation) to be in equilibrium. It is important that H-TDMA instruments include sufficient residence time to reach equilibrium for the system under study, so as to avoid under-predicting the measured growth factor.

It is thought that mixtures of different substances show mass transfer limitations due to inhomogeneous mixing or by forming of an organic film on the outside of the aerosol particles.

Further measurements are planned with laboratory mixtures with unusual equilibrium times. Secondary organic aerosol from the PSI smog chamber will also be studied. The equilibrium time for atmospheric aerosol for some locations will be determined.

ACKNOWLEDGEMENTS

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