The effects of organic compounds on the hygroscopic properties of inorganic aerosols

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The effects of organic compounds on the hygroscopic properties of inorganic aerosols

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for the degree of
Doctor of Sciences

presented by
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Prefazione

In atmosfera è presente materiale di natura organica sia sotto forma di gas che di materia condensata. Nelle ultime decadi sono state identificate e abbondantemente studiate le sorgenti naturali, come la vegetazione, e antropiche, come la combustione di biomassa e carburanti, di questo materiale. Lo studio degli effetti dei composti organici nelle particelle aerosol è importante per svariate ragioni: gli organici alterano la capacità di assorbimento di vapor acqueo da parte di aerosol inorganici (igroscopia), e perciò giocano un ruolo fondamentale nell'effetto indiretto degli aerosol sul budget radiativo del pianeta. Possono inoltre provocare limitazioni al trasferimento di massa tra la fase gassosa e condensata formando una pellicola sulla superficie delle particelle aerosol oppure complessificando la morfologia stessa della particella. Infini alterano le proprietà ottiche e la chimica eterogenea degli aerosol inorganici. Negli ultimi anni, una crescente attenzione è stata riservata al fine di comprendere come i composti organici influenzino l'igroscopia degli aerosol inorganici.

In questo studio sono state investigate le proprietà igroscopiche degli aerosol inorganici/organici per mezzo della tecnica del bilancio elettrodinamico (EDB). Il contenuto di questo lavoro è focalizzato principalmente sullo studio di due sistemi inorganici/organici: solfato d'ammonio / acido citrico (AS+CA) e solfato d'ammonio e acido adipico. Il solfato d'ammonio è il più importante componente inorganico degli aerosol atmosferici e le sue proprietà termodinamiche sono ben comprese e incluse nei modelli numerici. L'acido citrico e l'acido adipico sono composti organici con rispettivamente alta e bassa solubilità in acqua. Per il nostro studio questo significa che particelle di puro acido citrico rimangono liquide nell'EDB a qualsiasi umidità relativa, mentre quelle di puro acido adipico sono presenti in fase solida.

Sono stati compiuti numerosi cicli igroscopici (eseguiti variando l'umidità relativa da valori molto bassi a molto alti e viceversa) su queste particelle miste e i risultati sono stati analizzati e confrontati con i dati disponibili in letteratura. È stata riservata una speciale attenzione all'analisi del sistema AS+AA che beneficia dei risultati di uno
studio parallelo sugli aerosol misti inorganici/organici compiuto utilizzando un’altra
tecnica sperimentale, l’analizzatore igroscopico differenziale di mobilità’ montato in
tandem (H-TDMA). Per quanto riguarda il sistema AS+CA, le caratteristiche generali
si sono rivelate essere una depressione sia della umidità’ di cristallizzazione che di
quella di fusione del solfato d’ammonio e la presenza di un assorbimento di acqua
prima della fusione. Invece, il caso AS+AA mostra importanti effetti morfologici che
alterano la cinetica del sistema.

Inoltre, c’è stata sviluppata una nuova tecnica basata sulle risonanze ottiche di Mie
al fine di misurare bassissime pressioni di vapore di sostanze (come gli organici) in
aerosol acquosi; queste pressioni dipendono dall’umidità’ relativa e quindi dalla con-
centratazione della soluzione acquosa nella particella aerosol. I risultati di questa inves-
tigazione sono utili per calcolare la ripartizione gas-particella e particella-particella in
atmosfera e sono stati applicati al caso specifico dell’acido oxalico.
Abstract

Organic material is present in the atmosphere both in the gas phase and as condensed matter. Biogenic sources like vegetation, and anthropogenic ones like biomass burning and fossil fuel combustion have been identified and studied thoroughly during the last decades. The study of organic compounds in aerosol particles is important for several reasons: some organics take up water and affect the inorganic aerosol capability of uptaking it (hygroscopicity); hence, they play a role in the direct and indirect aerosol effect on the radiation budget of the earth. They may induce mass transfer limitations between gas and particle phase by forming a film on the particle surface, or by changing the morphology of the particles. In addition they alter the optical properties and the heterogeneous chemistry of inorganic aerosol particles.

In these last years, increasing attention has been paid to the understanding of how organic compounds affect the hygroscopicity of inorganic aerosols.

In this study the hygroscopic properties of inorganic/organic single aerosol particles have been investigated with an electrodynamic balance (EDB). Two inorganic/organic systems are the main subject of this work: ammonium sulfate / citric acid (AS+CA), and ammonium sulfate / adipic acid (AS+AA). Ammonium sulfate is a major inorganic component of atmospheric aerosols, and its thermodynamic properties are well understood and modelled. Citric acid and adipic acid are organic compounds with a high and low solubility in water, respectively. This causes a pure citric acid particle in the EDB to stay liquid at every relative humidity (continuous water uptake), whereas a pure adipic acid one is always solid (negligible water uptake).

Hygroscopicity cycles of these mixtures (with several mixing ratios of the solution) were performed and the results analyzed and compared with bulk and literature data. Special attention was paid to the analysis of the AS+AA mixture which benefit from the results of a companion study on inorganic/organic aerosol made with an hygroscopicity tandem differential mobility analyzer (H-TDMA).

For AS+CA mixtures the general features are a depression of both the deliquescence
and efflorescence relative humidities of AS and water uptake at low relative humidity, whereas the AS+AA case shows important morphology effects which alter the kinetics of the system.

In addition, a novel technique based on the analysis of Mie resonances of a particle in the EDB was developed in order to measure low vapor pressure of compounds (i.e. the organics) in aqueous solution particles, as a function of relative humidity, and hence on the concentration of the particle. The results of this investigation were also used for determining the gas-to-particle and particle-to-particle partitioning of oxalic acid in the atmosphere.
Chapter 1

Introduction

1.1 Motivation

It is well known that organic material is present in the atmosphere both in the gaseous phase and as condensed matter. It is also known that it is involved in many fundamental atmospheric and geobiochemical processes, spanning from the microphysics of clouds to global climate and geochemical cycles. Moreover, the monitoring of organic substances, some of them very harmful, is crucial for air quality issues, and so for human health. Despite all of this, less is known about the global sources, distribution and fluxes of organic matter than any other kind of chemical substances in the atmosphere. Aside maybe only from methane, the study of organic matter in the non urban atmosphere has to be considered rare and incomplete until the beginning of the 60s. The available thermodynamical data themselves are still scarce if compared with the inorganic counterpart, and the richness of the organic chemistry does not help the task of fulfilling the gap. Another problem is that the measurements of condensed matter in the atmosphere are also likely to be biased by the presence of organic material, and the laboratory study of some model organic substances leads to different results when performed with different techniques.

If we also consider that in the last two centuries a huge amount of organic matter have been injected in the atmosphere due to massive industrialization and global diffusion of fuel burning transportation, being the environmental consequences of this not well, or not at all, understood, then, there is no doubt that a better knowledge of the processes involving organic matter is required.

In these last years there has been growing interest in the study of the effects of organic material on the ability of taking up water by inorganic aerosol particles, because these
effects influence the light scattering properties of the particles, the cloud formation mechanism and the heterogeneous chemistry. The aim of this dissertation is to be a useful contribute to some aspects of the problem. Several mixed inorganic/organic systems are studied with the help of two instrumental setups: an electrodynamic balance and a hygroscopicity tandem differential mobility analyzer.

1.2 The atmosphere

Profiles. The atmosphere is the layer of gases surrounding the planet and retained by the gravity. It extends from the ground up to some hundreds of kilometers without a definite upper limit, but it slowly fades into empty space. It is a dynamical and chemical active system which underwent continuous and sometimes abrupt changes from its formation together with the Earth, something like 4.5 billion years ago, and it is still in evolution. The most practical way to represent the atmosphere is the temperature profile shown in Fig. 1.1, where the different layers correspond to regions of the atmosphere with remarkably different properties. The daily weather (clouds, rain, winds etc...) is practically completely confined in the lowest region, the troposphere, characterized by strong vertical convection, high level of water vapor and decreasing temperature with altitude. Up to 85% of the atmospheric mass is in this layer, which also contains most of the aerosol particles (see Section 1.3). The pressure profile shown in Fig. 1.1 is instead representative of the weight of the overlying column of air and it has an exponential decay which is followed by the density of air as well.

Composition. Of the 92 natural chemical elements, the major constituents of atmospheric composition are only nitrogen (N₂), oxygen (O₂), argon (Ar), and water vapor (H₂O). The other gases are present in the atmosphere at extremely low concentrations and are called trace gases, including carbon dioxide, neon, ozone, helium, methane, krypton, hydrogen, nitrous oxide. Despite their low concentrations, these trace gases can be of critical importance for the greenhouse effect, the ozone layer, smog formation, and other environmental issues. The mixing ratio concentration (i.e. mole of the gas to mole of air ratio) of these components, which is summarized in Table 1.1 and visualized in Fig. 1.2 is almost constant in the first 100km, apart from water vapor (almost entirely confined in the Troposphere) and ozone which have highly variable concentrations.

Dalton's law stipulates that each component of the air mixture must behave as if it were alone in the atmosphere. One might then expect mixing ratios to decrease with altitude.
1.2. The atmosphere

Figure 1.1: Vertical profiles of pressure and temperature for the standard atmosphere up to 80Km. Distinct layers are identified according to temperature changes with altitude. The lowermost layer, the Troposphere, contains the 80-85% of the weight of the atmosphere and almost the totality of particulate (and organic) matter.

Table 1.1: Concentration expressed as mixing ratio for the most abundant gaseous compounds in the atmosphere. Water is not included because can be approximated as a gas only far away from its saturation and its amount is highly variable with time and sampling location.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Mixing Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen (N₂)</td>
<td>0.78</td>
</tr>
<tr>
<td>Oxygen (O₂)</td>
<td>0.21</td>
</tr>
<tr>
<td>Argon (Ar)</td>
<td>0.0093</td>
</tr>
<tr>
<td>Carbon dioxide (CO₂)</td>
<td>365x10⁻⁶</td>
</tr>
<tr>
<td>Neon (Ne)</td>
<td>18x10⁻⁶</td>
</tr>
<tr>
<td>Ozone (O₃)</td>
<td>0.01-10x10⁻⁶</td>
</tr>
<tr>
<td>Helium (He)</td>
<td>5.2x10⁻⁶</td>
</tr>
<tr>
<td>Methane (CH₄)</td>
<td>1.7x10⁻⁶</td>
</tr>
<tr>
<td>Krypton (Kr)</td>
<td>1.1x10⁻⁶</td>
</tr>
<tr>
<td>Hydrogen (H₂)</td>
<td>500x10⁻⁹</td>
</tr>
<tr>
<td>Nitrous oxide (N₂O)</td>
<td>320x10⁻⁹</td>
</tr>
</tbody>
</table>
Figure 1.2: Diagrams summarizing the present atmospheric composition. It is clear that trace gases including volatile organics represent only a tiny part of the total amount contained in the unlabeled tiny slices of the lower pie. The chemical analysis is then in first analysis difficult, since very precise techniques are needed to characterize them.

However, gravitational separation of the air mixture takes place by molecular diffusion, which is considerably slower than turbulent vertical mixing of air for altitudes below 100 km. Turbulent mixing thus maintains a homogeneous lower atmosphere. Only above 100 km does significant gravitational separation of gases begin to take place, with lighter gases being enriched at higher altitudes.

Organic substances treated in this dissertation represent only a tiny amount of the gaseous matter present in our atmosphere.
1.3 Particulate matter (PM)

1.3.1 Sources and sinks

The word “aerosol” defines a two-phase system made up of the particles and the gas phase surrounding them. One has to consider the term particle like a conglomerate of molecules, from a few to billions of them, on a size scale from tens of nanometer to the centimeter. Particulate matter (PM) is the collective name for aerosol particles, even if the mere word “aerosols” is sometimes ambiguously used to refer to it.

It is ubiquitous in the lower atmosphere and can be found in a variety of shape and chemical composition. Mineral dust, rain droplets, fog, smog, smoke, soot, haze and debris are aerosol particles. Even a sample of “clean” atmospheric air (i.e. which does not belong to the visible phenomena like the ones just mentioned) normally contains a number of aerosol particles with concentration ranging from some hundreds to some thousands per cubic centimeter. Four examples of single aerosol particles are visualized in Fig. 1.3 and Fig. 1.4. Figure 1.3 shows electronic microscope pictures of organic debris: a pollen grain and brochosomas emitted in the atmosphere by vegetation and insects respectively. In Fig. 1.4 are instead displayed a salt particle typical of marine emissions and a soot particle originated from combusted diesel.

Aerosol particles can be classified according to the sources: the primary ones, directly emitted by biogenic or anthropogenic sources and the secondary ones, which are formed in the atmosphere after degradation of some precursors. The main sources of atmospheric aerosol particles can be categorized into the following types: (i) widespread surface sources of primary aerosols like arid soils (mineral dust), ocean (sea salt), biosphere (pollen), biomass and fuel burning (soot); (ii) diffuse sources within atmospheric volume as air traffic, secondary aerosols from chemical degradation of volatile compounds; (iii) intense point sources like volcanoes; extraterrestrial sources (usually neglected). A global budget of the emission fluxes is summarized in Tab. 1.2. Natural sources dominate the global aerosol emissions, but in urban areas the relative anthropogenic contribution becomes much more important. The lifetime of aerosol particles is between few hours to some weeks, a time long enough to allow long-range transport. As a result of multiple sources and relatively short lifetime compared with a number of trace gases, the major feature of aerosols is their variability and heterogeneity in time and space.

The two pieces of information necessary to characterize particulate matter are size distribution (or alternatively, area or volume distribution) and chemical composition.
Chapter 1. Introduction

Figure 1.3: Directly emitted organic particles: a pollen grain on the left and brochosomas on the right (secretory granules produced by some insects). Source: M. O. Andreae and MPI, Mainz.

Figure 1.4: Model aerosol particles. On the left, a sodium chloride salt crystal, typical of marine aerosols (sea spray) emitted at water surface. On the right, a soot particle common in exhausted emissions.

The latter will be exposed in Section 1.6.3. Figure 1.5 shows instead a theoretical surface area distribution and summarizes the main sources, sinks, and processes related to aerosols. Ultrafine aerosol particles (less than 0.01 μm in radius) originate almost exclusively from nucleation (clustering of molecules) and condensation of precursor gases (H₂SO₄, NH₃, HNO₃, organics), while coarse particles (1-10 μm in radius) are emitted by mechanical action of the wind on the Earth’s surface. The fine particles between 0.01 and 0.1 μm have multiple sources, from coagulation (adhesion after collisions) of smaller particles to direct condensation of vapors. They tend to remain in the size range called accumulation mode, because they are too large to grow rapidly by condensation, and because the slower random motion of large particles reduces the coagulation rate. On the other hand they are still too small for gravitational deposition (also called dry deposition) to play a significant role. The main sink is thus the wet
1.4 Aerosol-Climate interactions

Table 1.2: Sources and global emission estimates for atmospheric aerosols. The biogenic photochemical source is primarily particle formation from isoprene and monoterpene vapors from vegetation, while the anthropogenic photochemical item is primarily particle formation from anthropogenic volatile organic compounds. Source: Aerosol Technology [1].

<table>
<thead>
<tr>
<th>Source</th>
<th>Amount Tg/y Best Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Biogenic</strong></td>
<td></td>
</tr>
<tr>
<td>Soil dust</td>
<td>1500</td>
</tr>
<tr>
<td>Sea salt</td>
<td>1300</td>
</tr>
<tr>
<td>Botanic debris</td>
<td>50</td>
</tr>
<tr>
<td>Volcanic dust</td>
<td>30</td>
</tr>
<tr>
<td>Forest fires</td>
<td>20</td>
</tr>
<tr>
<td>Gas-to-particle conversion</td>
<td>180</td>
</tr>
<tr>
<td>Photochemical</td>
<td>60</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>3100</strong></td>
</tr>
<tr>
<td>** Anthropogenic**</td>
<td></td>
</tr>
<tr>
<td>Direct emissions</td>
<td>120</td>
</tr>
<tr>
<td>Gas-to-particle conversion</td>
<td>330</td>
</tr>
<tr>
<td>Photochemical</td>
<td>10</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>460</strong></td>
</tr>
</tbody>
</table>

deposition through washout by clouds. Dry and wet deposition are both important sinks for the coarse mode.

1.4 Aerosol-Climate interactions

The earth's average temperature and climate results from the distribution and transformation of the incoming solar radiation. Perturbation of this energy budget can induce a climate change. The aerosol radiative forcing is defined as the modification of the terrestrial radiative budget due to the presence of aerosols caused by the present human activities, compared to a preindustrial situation (1750). Aerosols have perturbing effects and these perturbations occur both directly following particle-radiation interactions (direct aerosol effect), and indirectly through cloud processes (indirect aerosol effect). Aerosol particles are capable of scattering the short wave radiation coming from the sun and the longwave radiation coming from the ground. They also show
Figure 1.5: Theoretical area distribution of aerosol particles as in Whitby [2]. Three definite modes or range of distribution are distinguishable in correspondence of the maxima. Related to them are different sources and sinks. While a particle can pass from the nuclei mode to the accumulation mode, the next step to the coarse mode is generally prohibited for physical reason. See text for details.

Absorbent behavior depending on their chemical composition. One big question to be considered is that, at comparable concentrations, secondary anthropogenic aerosols are much more effective than biogenic ones concerning the absorbance and scattering of radiation. If the absorbance is very high, like in the case of black carbon aerosol particles, the local heat produced can then lead to an evaporation of the clouds and to a warming of the climate (this is called semi-direct effect).

The indirect effects are instead related to clouds, which on average cover the 65% of the earth. Aerosol particles play the role of cloud condensation nuclei (CCN). More CCN, for a given amount of condensable water vapor, induce the formation of more small droplets which increase the cloud reflectivity (first indirect effect) and decrease...
1.5 Human health

the precipitation which increase cloud cover (second indirect effect).

As can be seen in Fig. 1.6 aerosol particles have a negative forcing (cooling), called the “whitehouse” effect, by contrast with the greenhouse effect related to trace gases. Fig. 1.6 and 1.7 (a readaptment) quantify the different contributions to the radiative earth budget perturbations. The figure is taken from the the 2001 report of the Intergovernmental Panel on Climate Change (IPCC report 2001 [3]).

![Diagram](image)

Figure 1.6: The different contributions to the radiative forcing versus the level of comprehension. Aerosol particles have a potential strong negative forcing through the indirect effect explained in the text. The uncertainty though, is of the same order of the forcing. Organic carbon and black carbon have instead a better assessment and a counteracting effect. The forcing is calculated comparing the present day situation to a preindustrial one (year 1750), and so all of the contributions are anthropogenic apart from the last one, the change in the solar input. Source: IPCC report 2001 [3]

1.5 Human health

Air pollution has been associated with adverse health effects like pulmonary inflammation, thrombosis and cancer since many years. In the early 18th century, the Italian physician Bernardo Ramazzini, a founder of occupational/industrial medicine, recorded his observations associating respiratory disorders with worker exposure to dusts from vegetable fibers and grain. The book “De morbis artificum diaetribae” [4] (see Fig. 1.8) outlines the health hazards of irritating chemicals, dust, metals, and
other abrasive agents encountered by workers in 52 occupations. Among them were miners, potters, masons, wrestlers, farmers, nurses, soldiers, and many others. A first tragic evidence of the social hazard associated with air pollution became clear during this century. Between 1 and 5 December 1930, a persistent fog affected a narrow valley along the Meuse river in Belgium. This area was one of the most industrialized in continental Europe. More than 60 people died and many others suffered of severe respiratory problems. A committee of experts concluded that emissions of SO₂ and fine particles, which could not be removed from the valley because of a persistent temperature inversion (and hence inhibited air convection), were responsible for this tragedy. Micron sized pure carbon particles were observed in lung autopsies. This is the first scientific demonstration of mortality or morbidity caused by particulate air pollution. The warnings of the committee about the likelihood of similar conditions in that and other industrialized regions did not avoid what happened in London in 1952, again in winter, when more than 3000 people died after a dense fog covered the city for several days [5]. Apart from these two extreme events, air pollution is however responsible or co-responsible of thousands of hospitalizations or deaths every year around the globe, representing a major problem for modern societies.

Figure 1.7: Readaptation of Fig. 1.6 with in evidence the direct and indirect effect of aerosols. While it is clear that black carbon causes a positive forcing due to its strong absorbance, organic carbon is more subtle and not reported given that it can have absorbance capability but also a high tendency to uptake water and act as good CCN for cloud formation.
1.5. Human health

Figure 1.8: The first scientific publication associating respiratory disorders with worker exposure to dusts from vegetable fibers and grain.

1.5.1 Deposition

Particle size and chemical composition are the two main properties governing the behavior of particles in the respiratory tract (see Fig. 1.9). The deposition occurs mainly via inertial impactation, sedimentation and Brownian diffusion. The inertial impactation, which is the most important process in the upper airways, is a flow dependent mechanism involving mainly large particles (> 5μm). The higher the particle size and flow velocity, the higher the probability for the particle to exit the flow lines and impact on the surfaces. Sedimentation occurs in the lower airways for medium particle size (1-5μm), it is governed by gravity and its efficiency depends on the size of the particle and the residence time. Brownian motion (random movements of the aerosol particles due to the kinetics of the gaseous medium in which they are suspended), which is well described in [1] is predominant for ultrafine particles (< 0.1μm). A fraction of ultrafine particles can translocate directly into the blood.

1.5.2 Short-term and long-term effects

There are numerous studies demonstrating the short-term and long-term effects of particulate air pollution like the famous one from Dockery and Pope [7] or the brilliant book by Holgate et al. [9]. Summarizing the short-term damage, they show that a 10μg/m³ increase in PM₁₀ (particle size less than 10μm) is associated with a 0.8%
increase in total daily mortality, a 3% and a 1.5% in respiratory and cardiovascular mortality respectively. About the long-term influences, a 6% and 9% for total and cardiopulmonary mortality are related to a 10\(\mu g/m^3\) increase in PM\(_{2.5}\) respectively. Scientific evidences that pollution reduction is directly related to improved respiratory health can be found in a Swiss study by Bayer-Oglesby et al. [6]. The relevance of this health problem is better understood if instead of a individual relative risk of exposure to particulate air pollution an “attributable risk” is taken into account. This index includes the number of people exposed to the exposure distribution in the population. The problem was studied in an international project involving several European cities which has been published by Koistinen [10].

### 1.6 Organic material

#### 1.6.1 Introduction

Organic materials exist in the atmosphere in two phases: as a gas phase and as particulate matter. The latter can originate from direct emissions (Primary Organic Aerosols, POA) or can be formed in the atmosphere as secondary aerosol (SOA) from organic reaction products undergoing phase transition processes. Both phases have biogenic
1.6. Organic material

In literature, many acronyms defining the organic materials in the atmosphere can be found and their number is related to the complexity of organic chemistry. A first separation of the total carbon TC present in the atmosphere is between elemental carbon EC, black non-volatile carbon which have a chemical structure similar to impure graphite (also called soot) and organic carbon OC, which can be divided in volatile and particulate compounds, VOC and POC. According to their biogenic or anthropogenic sources, their oxygenated nature, their reactivity, or their water solubility, volatile organic compounds (OC) can develop further in OVOC, ORVOC or WSOC. Often the non-methane nature of total hydrocarbons is stressed as TNMHC. Perhaps less is known about global sources, distribution, and fluxes of organic matter (apart from methane) than any other major class of chemical substances in the atmosphere. For instance only from 1960 there has been significant interest in the organic chemistry of nonurban atmosphere and the effect of anthropogenic organic emissions on natural atmospheric processes. The work of Went [15] first suggested the potential importance of vegetation as a major source for atmospheric hydrocarbons. He also suggested that vapor phase terpenes emitted from certain types of vegetation rapidly undergo reactions to form condensed phase particles, the bluish haze often observed over and near forested areas (see Fig. 1.11). These organically derived blue hazes have potential important effects on the atmospheric radiation budget, but in general the rela-

Figure 1.10: Particulate air pollution. Short term effects of PM$_{10}$. Estimated % change in daily mortality per 10 $\mu$g/m$^3$ increase in PM$_{10}$. In Holgate 1999 [9].
Figure 1.11: Bluish haze observed over some forests. It is produced by gas to particle conversion of compounds emitted by vegetation.

The interaction between the organic content of atmospheric particles and their optical properties is poorly known [17]. Some organics (mainly from anthropogenic origin, like the PAHs, polycyclic aromatic hydrocarbons or PCBs, polychlorinated biphenyls) are hazardous and since year 1980 attention has been paid to their long distance transport, given the rather low but uniform concentrations found in soils and marine sediments. In addition, water soluble organics affect the hygroscopicity (water uptake) of particulate matter for instance depressing the deliquescence [16], and thus they play a role in the formation of clouds, and in the evaporation and growth of water droplets [17], [18], [19]. Organics can also act as a film on aerosol particles and cause a mass transfer delay between gas and particle phase [20]. Finally, it is clear that organics impacts upon many fundamental geochemical cycles, like the one of tropospheric ozone, or the halogens cycles (chlorine, bromine, iodide) [12].

Figure 1.12 summarizes schematically the cycle of organic compounds in terms of biogenic sources (vegetation and ocean), anthropogenic sources (biomass burning, fossil fuel combustion, industries), sinks (dry and wet deposition), and oxidation patterns leading to formation of secondary organic aerosols.

1.6.2 Vapor phase organic material

Volatile organic compounds (VOC), which include non-methane hydrocarbons (NMHC) and oxygenated NMHC (e.g., alcohols, aldehydes and organic acids), have short at-
1.6. Organic material

![Figure 1.12: Schematic summarizing the main sources and sinks of organic matter, and the gas to particle conversion of VOC in secondary organic aerosols (SOA).](image)

Atmospheric lifetimes (fractions of a day to months) and small direct impact on radiative forcing. VOC influence climate through their production of organic aerosols and their involvement in photochemistry, i.e., production of O₃ in the presence of NOx and light. The largest source, by far, is natural emission from vegetation. Isoprene, with the largest emission rate, is not stored in plants and is only emitted during photosynthesis.

Isoprene emission is an important component in tropospheric photochemistry [21]. Monoterpenes are stored in plant reservoirs, so they are emitted throughout the day and night. The monoterpenes play an important role in aerosol formation. Vegetation also releases other VOC at relatively small rates, and small amounts of NMHC are emitted naturally by the oceans. Anthropogenic sources of VOC include fuel production, distribution, and combustion, with the largest source being emissions from motor vehicles due to either evaporation or incomplete combustion of fuel, and from biomass burning. Thousands of different compounds with varying lifetimes and chemical be-

<table>
<thead>
<tr>
<th>Source</th>
<th>Total</th>
<th>Isoprene</th>
<th>Terpene</th>
<th>Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fossil fuel</td>
<td>161</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>33</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Vegetation</td>
<td>377</td>
<td>220</td>
<td>127</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 1.3: Estimates of global VOC emissions (in TgC/yr) from different sources as in IPCC report 2001 [3].
havior have been observed in the atmosphere. Generally, fossil VOC sources have already been accounted for as release of fossil C in the CO₂ budgets and thus VOC are not counted as a source of CO₂. Given their short lifetimes and geographically varying sources, it is not possible to derive a global atmospheric burden or mean abundance for most VOC from current measurements. VOC abundances are generally concentrated very near their sources. Natural emissions occur predominantly in the tropics (23°S to 23°N) with smaller amounts emitted in the northern mid-latitudes and boreal regions mainly in the warmer seasons. Anthropogenic emissions occur in heavily populated, industrialized regions (95% in the Northern Hemisphere peaking at 40°N to 50°N), where natural emissions are relatively low, so they have significant impacts on regional chemistry despite small global emissions. A few VOC, such as ethane and acetone, are longer lived and impact tropospheric chemistry on hemispheric scales. Table 1.4 shows two different estimates of the global emissions. It is expected that anthropogenic emissions of most VOC have risen since preindustrial times due to increased use of gasoline and other hydrocarbon products. Due to the importance of VOC abundance in determining tropospheric O₃ and OH, systematic measurements and analysis of their budgets will remain important in understanding the chemistry-climate coupling.

1.6.3 Organic Aerosols

Organic compounds make up a large but highly variable fraction of the atmospheric aerosol. Organic aerosol particles are directly emitted, biogenically by vegetation and by the ocean, and anthropogenically by fossil fuel and biomass burning, and by industries. Together with this particulate emissions a gas phase emission is present and the degradation of these precursors through oxidation leads to secondary aerosols formation. An estimate of the production rate according to the different sources for these organic aerosols is summarized in Tab. 1.5. The anthropogenic impact is evident in

<table>
<thead>
<tr>
<th>Table 1.4: Estimates of global VOC emissions (in TgC/yr) from different sources as in IPCC report 2001 [3].</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Source</strong></td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>Fossil fuel</td>
</tr>
<tr>
<td>Biomass burning</td>
</tr>
<tr>
<td>Vegetation</td>
</tr>
</tbody>
</table>
Organic material

the major contribution, biomass burning. Anyway, as explained below in detail, even the SOA from biogenic origin are anthropogenically influenced. The chemical composition of aerosol particles is highly variable depending on geographic location. Figure 1.13 summarizes aerosol composition measurements for aerosol particles smaller than 2.5\(\mu\)m in diameter (fine particles) in United State, Canada and Mexico. The location, total mass, and specification are reported for every sampling station. It can be seen that the organic component is between 20 and 40%, in some single measurements (not reported) up to 90%.

Organics are the largest single component of biomass burning aerosols [22]. Measurements over the Atlantic in the haze plume from the United States indicated that organic aerosols scattered at least as much light as sulphate particles. Organics are also important constituents, perhaps even a majority, of upper-tropospheric aerosols and there are indications of their existence in the lower stratosphere [23]. The presence of polar functional groups, particularly carboxylic and dicarboxylic acids, makes many of the organic compounds in aerosols water soluble. This affects the water uptake of aerosols particles [60] and allows them to participate in cloud droplet nucleation [19]. Recent field measurements have confirmed that organic aerosols may be efficient cloud nuclei and consequently play an important role for the indirect climate effect as well [25].

There are significant analytical difficulties in making valid measurements of the various organic carbon species in aerosols. Figure 1.14 shows how these difficulties affect the characterization of fine aerosol particles using high resolution gas chromatography.

<table>
<thead>
<tr>
<th>Type of source</th>
<th>Tg/y</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Primary</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Organic aerosol (0 - 2(\mu)m)</strong></td>
<td></td>
</tr>
<tr>
<td>Biomass Burning</td>
<td>54</td>
</tr>
<tr>
<td>Fossil fuel</td>
<td>28</td>
</tr>
<tr>
<td>Biogenic (&gt; 2(\mu)m)</td>
<td>56</td>
</tr>
<tr>
<td><strong>Black carbon</strong></td>
<td></td>
</tr>
<tr>
<td>Biomass burning</td>
<td>5.7</td>
</tr>
<tr>
<td>Fossil fuel</td>
<td>6.6</td>
</tr>
<tr>
<td><strong>Secondary (SOA)</strong></td>
<td></td>
</tr>
<tr>
<td>Biogenic VOC</td>
<td>16</td>
</tr>
<tr>
<td>Anthropogenic VOC</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table 1.5: Emission burdens for organic aerosols, with separate contributions for black and organic carbon. Source: IPCC report 2001 [3].
Chapter 1. Introduction

Figure 1.13: Composition of PM2.5 at representative urban and rural locations. Averaging periods and average PM2.5 mass are indicated. Source: NARSTO report [14].

(HRGC) and gas chromatography/mass spectrometry (GC/MS) techniques [26]. While over the 40% of the total aerosol mass can be allocated as carbonaceous material (fossil black carbon plus organic carbon), only half of the organic carbon component can be extracted with these techniques. In addition, HRGC and GC/MS-chromatograms produced from urban aerosol samples usually contain a large number of branched and cyclic hydrocarbons. These hydrocarbons are derived mainly from fossil fuel utilization and produce an unresolved accumulation of compounds in the chromatograms. Hence, the mass of extractable organics can be subdivided further into resolved (individual peaks) and unresolved organic components. The resolved portion comprises about 23-29% of the elutable organic mass. From this resolved portion, only about 75-85% can be identified as single molecular entities. It is evident that a large part of the organic component can not be either extracted or resolved. Large artifacts can be produced by both adsorption of organics from the gas phase onto aerosol collection media, as well as evaporation of volatile organics from aerosol samples. Progress has been made on minimizing and correcting for these artifacts through several techniques, but no rigorous comparisons of different techniques are available to constrain measurement errors.

One of the aim of this dissertation is also to compare two different common techniques
for characterizing the hygroscopicity of aerosol particles, the electromagnetic balance and the differential mobility analyzer. In Chapters 4 and 5 and in the Appendices some light is shed on the problem.

Of particular importance for the direct effect is the light absorbing character of some carbonaceous species, such as soot and tarry substances [27]. Modeling studies suggest that the abundance of "black carbon" relative to non-absorbing constituents has a strong influence on the magnitude of the direct effect. Given their importance, measurements of black carbon, and the differentiation between black and organic carbon, still require improvement. Even gas phase organics absorbed by aerosol particles can strongly alter the scattering properties as shown in App. A, where the effects of formaldehyde uptake on sulfuric acid particles are studied.

**Biomass and fuel burning.** The main sources for carbonaceous aerosols in the submicron size are biomass and fossil fuel burning (see Tab. 1.5. The global emission of organic aerosol from biomass and fossil fuel burning has been estimated at 45 to 80 and 10 to 30 Tg/yr, respectively [28], [29], [30]. Combustion processes are the dominant source for black carbon as well. Recent estimates place black carbon global emissions from biomass burning at 6 to 9 Tg/yr and from fossil fuel burning at 6 to 8 Tg/yr [31], [28], [30]. The source distribution for organic and black aerosols from these sources are shown in Fig. 1.15 and Fig. 1.16 where maxima correspond to industrialized regions together with agricultural and forest sites experiencing heavy biomass burning.

Substantial progress has been made in recent years with regard to the emission factors, i.e., the amount of aerosol emitted per amount of biomass burned. In contrast, the
estimation of the amounts of biomass combusted per unit area and time is still based on rather crude assessments and has not yet benefited significantly from the remote sensing tools becoming available. Where comparisons between different approaches to combustion estimates have been made, they have shown differences of almost an order of magnitude for specific regions.

**Oxidation of hydrocarbons** Atmospheric oxidation of biogenic hydrocarbons yields compounds of low volatility that readily form aerosols. Because it is formed by gas-to-particle conversion, this secondary organic aerosol (SOA) is present in the sub-micron
1.6. Organic material

size fraction. Lioussé et al. [28] included SOA formation from biogenic precursors in their global study of carbonaceous aerosols; they employed a constant aerosol yield of 5% for all terpenes. Based on smog chamber data and an aerosol-producing VOC emissions rate of 300 to 500 TgC/yr, Andreae and Crutzen [32] provided an estimate of the global aerosol production from biogenic precursors of 30 to 270 Tg/yr. Recent analyses based on improved knowledge of reaction pathways and non-methane hydrocarbon source inventories have led to substantial downward revisions of this estimate. The total global emissions of monoterpenes and other reactive volatile organic compounds (ORVOC) have been estimated by ecosystem by Guenther et al. [21]. By determining the predominant plant types associated with these ecosystems and identifying and quantifying the specific monoterpene and ORVOC emissions from these plants, the contributions of individual compounds to emissions of monoterpenes or ORVOC on a global scale can be inferred [33]. Experiments investigating the aerosol-forming potentials of biogenic compounds have shown that aerosol production yields depend on the oxidation mechanism. In general, oxidation by O₃ or NO₃ individually yields more aerosol than oxidation by OH [34]. However, because of the low concentrations of NO₃ and O₃ outside of polluted areas, on a global scale most VOC oxidation occurs through reaction with OH. The subsequent condensation of organic compounds onto aerosols is a function not only of the vapour pressure of the various molecules and the ambient temperature, but also the presence of other aerosol organics that can absorb products from gas-phase hydrocarbon oxidation [35].

This dissertation will include an entire chapter (Chapter 3) about vapor pressure measurements of organic compounds. When combined with appropriate transport and reaction mechanisms in global chemistry transport models, these hydrocarbon emissions yield estimated ranges of global biogenically derived SOA of 13 to 24 Tg/yr and 8 to 40 Tg/yr.

It should be noted that while the precursors of this aerosol are indeed of natural origin, the dependence of aerosol yield on the oxidation mechanism implies that aerosol production from biogenic emissions might be influenced by human activities. Anthropogenic emissions, especially of NOx, are causing an increase in the amounts of O₃ and NO₃, resulting in a possible 3- to 4-fold increase of biogenic organic aerosol production since pre-industrial times [36]. Recent studies in Amazonia confirm low aerosol yields and little production of new particles from VOC oxidation under unpolluted conditions. Given the vast amount of VOC emitted in the humid tropics, a large increase in SOA production could be expected from increasing development and anthropogenic emissions in this region.
Anthropogenic VOC can also be oxidised to organic particulate matter. Only the oxidation of aromatic compounds, however, yields significant amounts of aerosol, typically about 30 g of particulate matter for 1 kg of aromatic compounds oxidised under urban conditions [35]. The global emission of anthropogenic VOC has been estimated at 109 ± 27 Tg/yr, of which about 60% is attributable to fossil fuel use and the rest to biomass burning [37]. The emission of aromatics amounts to about 19 ± 5 Tg/yr, of which 12 ± 3 Tg/yr is related to fossil fuel use. Using these data, we obtain a very small source strength for this aerosol type, about 0.6 ± 0.3 Tg/yr. Fig. 1.17 shows the emission of these biogenically derived aerosol.

![Figure 1.17: Global distribution of SOA production from biogenic precursors, mainly terpene. Source: IPCC 2001 [3].](image)

**Primary biogenic aerosols.** Primary biogenic aerosol consists of plant debris (cuticular waxes, leaf fragments, etc.), humic matter, and microbial particles (bacteria, fungi, viruses, algae, pollen, spores, etc.). Unfortunately, little information is available that would allow a reliable estimate of the contribution of primary biogenic particles to the atmospheric aerosol. In an urban, temperate setting, Mathias-Maser and Jaenicke [38] have found concentrations of 10 to 30% of the total aerosol volume in both the sub-micron and super-micron size fractions. Their contribution in densely vegetated regions, particularly the moist tropics, could be even more significant. The presence of humic-like substances makes this aerosol light-absorbing, especially in the UV-B region, and there is evidence that primary biogenic particles may be able to act both as cloud droplet and ice nuclei. They may, therefore, be of importance for both direct and indirect climatic effects, but not enough is known at this time to assess their role with any confidence. Since their atmospheric abundance may undergo large changes as a
result of land-use change, they deserve more scientific study.

For a complete and detailed report on carbonaceous aerosols one could refer to the publication by Gelencser [39] and Seinfeld [40]. Kanakidou recently published a long detailed report which analyzes all the problematics involved in SOA modeling [41].
Chapter 2

Methodology

The experimental setup used in our experiments is described in detail elsewhere [42]. A schematic representation of the main features of the apparatus is shown in Fig. 2.1. An electrically charged particle (typically 2-20 μm in diameter) is balanced in an electrodynamic trap [43]. The balance is hosted within a three wall glass chamber with a cooling agent flowing between the inner walls and an insulation vacuum between the outer walls. The temperature can be varied between 330 and 160 K with a stability better than 100 mK and an accuracy of ±0.5 K. A constant flow (typically 30 sccm) of a N₂/H₂O mixture with a controlled H₂O partial pressure is pumped continuously through the chamber at a constant total pressure adjustable between 200 and 1000 mbar. During an experiment, the temperature is kept constant and the relative humidity within the chamber is increased or decreased continuously by changing the N₂/H₂O ratio, using automatic mass flow controllers. The relative humidity is registered by a capacitive thin film relative humidity sensor (MiniCap 2, Panametrics, U.S.A.) that is mounted in close vicinity of the levitated particle (< 10mm). The sensor was calibrated directly in the trap using the deliquescence relative humidity of different salts. Its accuracy is (1.5% RH between 10 and 90% RH. A single-particle generator (Hewlett-Packard 51633A ink jet cartridge) is used to inject a liquid particle under ambient laboratory conditions. After closing the chamber, temperature and relative humidity are set as explained above.

Five independent analytical tools provide information on the particle: (i) mass from DC voltage, (ii) radius from Mie phase function analysis, (iii) composition from Raman spectroscopy, and (iv) particle shape and morphology from intensity fluctuation measurements, (v) radius from optical resonances. These techniques are applied as follows.
Figure 2.1: The electrodynamic trap at the Institute for Atmospheric and Climate Science (IAC-ETH) in Zurich. Four metal rings (the electromagnetic balance) provide the oscillating and constant electric fields necessary to keep the aerosol particle levitating against the gravitational force. Two lasers illuminate the particle from below and the scattered light is collected in the near and far optical field by two CCD cameras. CCD1 is used to provide the optical signal for the automatic feedback of the DC field to adjust for changes in the gravitational force. CCD2 shows the far field pattern of the scattered light which is used for sizing the particle when spherical and optically homogeneous (e.g. in the case of a liquid one). The intensity of the scattered light is also monitored in a small scattering angle at about 90° by a photomultiplier (PMT), and an optical multichannel analyzer is used for Raman spectroscopy.

(i) Two collinear laser beams illuminate the levitated particle from below (HeNe: 632.8 nm, 3 mW. Ar⁺: 488.0 nm, 400 mW). The video image of the particle on CCD 1 and an automatic feedback loop are used to adjust the DC voltage for compensating the gravitational force [44]. A change in DC voltage is a direct measurement for the particle's mass change and, if the gas phase contains only water vapor, its concentration change.

(ii) The fringe pattern (measured with CCD 2) of the elastically scattered light of both lasers is compared with Mie theory to deduce the radius of a liquid particle (see Fig. 2.2 and 2.3) [45]. After a liquid-to-solid transition occurs, the fringe pattern loses its regular, periodic structure, and thus no meaningful radius values can be obtained for solid particles if their shape deviates strongly from being spherical.

(iii) Raman spectroscopy, using the Ar⁺ laser as an excitation source in a 90° scattering
Figure 2.2: Two-dimensional angular scattering pattern of an ammonium sulfate aerosol particle registered by the CCD2 camera. When the particle is completely liquid and homogeneous a fringe pattern appears (left and middle pictures obtained with HeNe and Ar+ respectively). An automatic algorithm measures the mean distance between the fringes and the radius is thus calculated (see text). The picture on the right shows the irregularly scattered light from the particle in the solid phase. No calculation of the radius is possible in this case.

Figure 2.3: Mie calculations for light scattering angles between 78° and 101°. The scattering angle difference between fringe maxima is plotted against the Mie parameter (left graph) for two refractive indices (1.36 for water and 1.48 for sulfuric acid). The inverse of this difference is almost linear against the Mie parameter (right graph). It is evident that the choice of the size parameter (hence, the particle size) associated with the scattering angle difference is affected by an intrinsic uncertainty.

geometry without an analyzing polarizer is performed to identify the chemical composition of the particles. Two holographic notch filters are used to reject the elastically scattered light of both lasers, and an optical fiber is employed to deliver the Raman-shifted light to a 150 mm spectrograph with a slow scan back-illuminated CCD array detector.

(iv) A photomultiplier with a relatively small conical detection angle (approximately 0.2° half-angle) is then used to measure the scattering intensity at 90° to the incident
beam and feed this signal to an analogue lock-in amplifier to measure the intensity fluctuations, that is, the root mean square deviation from the intensity mean [47]. Because of its symmetry, a homogeneous spherical particle will show a constant scattering intensity and hence a very small fluctuation amplitude. A nonspherical particle will scatter light with different intensity in the detection angle depending on its orientation relative to the incoming laser beam. (All particles perform Brownian rotational motion in an electrodynamic balance). These intensity fluctuation amplitudes have been previously used also to characterize liquid microdroplets with a single solid inclusion [48].

(v) A ball-lens LED with high degree of spatial coherence is used as a “white” light source to excite the Morphology Dependent Resonance (MDR) spectra of the particle [49] [50] [51]. The spectra recorded by an Optical Multichannel Analyzer are used to estimate very small radius changes and this information can be applied for instance to measure the vapor pressures of the particle constituents. This technique together with its application is described in detailed in a paper by the author of this dissertation and colleagues [52] which is integrally reported in Chap. 3.

Figure 2.4 shows the time-dependent raw data of a typical experiment with an aerosol particle with known $(NH_4)_2SO_4/H_2O$ ratio. The lowermost panel shows the DC voltage compensating the gravitational force (black curve) and the relative humidity (RH) measured in the trap (red curve) by a capacitive thin film sensor that is mounted in close vicinity of the levitated particle (<10 mm). The middle panel shows the root mean square deviation (RMSD) of the scattering intensity, which qualitatively characterizes the deviation from a perfect sphere and therefore the morphology of an aerosol particle. Small values (rms < 0.05) correspond to spherical droplets, whereas large values (rms > 1) correspond to very aspherical particles. The uppermost panel shows the particle radius, which is calculated with Mie phase function analysis [45] for the two different laser wavelengths (λ= 633 nm and λ = 488 nm). For aspherical, that is solid or mixed-phase particles, Mie phase function analysis provides noisy data (see scatter) with very distinct transitions from spherical to aspherical and back [46].

During this particular experiment a solid $(NH_4)_2SO_4$ aerosol particle is humidified. It deliquesces at $t \approx 22000$ s, RH about 79% (Deliquescence Relative Humidity, DRH) and takes up further water until the RH reaches about 85%. The RH was subsequently decreased ($t \approx 30000$s) and water evaporates continuously. Once the $RH < DRH$ ($t > 35000$s), the particle is supersaturated and the hysteresis region is reached. Eventually, the crystal effloresces at $t \approx 45000$ s, RH≈40% (Efflorescence Relative Humidity, ERH) and loses all its remaining water spontaneously. Further decrease in RH does not result in any further changes of DC voltage or rms values.
Figure 2.4: Temporal evolution of a typical experiment with the particle trap. Lowermost panel: relative humidity (red curve) and DC voltage proportional to the particle mass. Middle panel: The light intensity fluctuation data give information about the asphericity of the particle (see text). Uppermost panel: optical radius from fringe patterns described in Fig. 2.2.

Figure 2.5 shows the humidogram built with the raw data in the lower panel of Fig. 2.4. The voltage versus RH shows evidently the transitions from solid to liquid phases and back and the water cycle hysteresis typical of inorganic salts. The maximum absolute errors in the temperature, radius, and $U_{DC}$ are $\Delta T = 0.35K$, $\Delta r = 0.25 \mu m$, and $\Delta U_{DC} = 0.5 V$, respectively.
Figure 2.5: Humidogram of an ammonium sulfate aqueous solution aerosol particle, \( r \approx 5 \mu m \) at ambient temperature. The main features are labeled: solid phase till the deliquescence point (RH = 80%); abrupt solid to liquid phase transition; liquid state up to RH = 92% and down to RH = 40%; liquid to solid phase transition (efflorescence).
Chapter 3

White light spectroscopy

This chapter is the paper published by the author of this dissertation on Optics Express.
“White light Mie resonance spectroscopy used to measure very low vapor pressures of substances in aqueous solution aerosol particles”

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3.1 Abstract

We report a novel and fairly simple optical technique for sizing and measuring the evaporation rates of aqueous solution aerosol particles. A ball-lens LED with high degree of spatial coherence is used as a “white” light source to excite the Morphology Dependent Resonance (MDR) spectra of a microdroplet levitated in an electrodynamic balance (EDB). The spectra are recorded by an Optical Multichannel Analyzer. We show that very low vapor pressures of substances in aqueous solution particles can be measured for different temperatures and relative humidities (hence for different concentrations). As an application we measured the vapor pressure and the enthalpy of vaporization of aqueous malonic acid, a substance of interest for atmospheric science.

3.2 Introduction

Low vapor pressures are difficult to measure in general, and it is especially challenging to perform measurements at low temperatures typical for aerosol particles under upper tropospheric conditions.

Amongst the many different substances present in atmospheric aerosols, in this paper we focus on oxygenated organic compounds (e.g. dicarboxylic acids) of very low vapor pressures. They originate from direct emissions as well as from photochemical reactions of biogenic and anthropogenic precursors. There is considerable interest in understanding the formation but also the partitioning between gas and particle phase of these compounds because of their influence on atmospheric chemistry and the radiative properties of the aerosol [3]. In order to predict the partitioning it is important to know the vapor pressure of the compounds and its dependence on temperature and composition of the aerosol [53]. If the compounds are water soluble like the dicarboxylic acids, they will form an aqueous solution in the condensed aerosol phase and the concentration of the organic acid and its vapor pressure will depend on relative humidity.

A possible approach to determine vapor pressures is to measure evaporation rates of aerosol particles of known composition at fixed temperatures and relative humidities. One way for measuring evaporation rates of aerosol particles is by using the Tandem Differential Mobility Analyzer (TDMA) [3].

In the case of very low vapor pressures, this technique is limited by the finite residence time (some seconds) of the aerosol particles in the laminar flow tube. Alternatively,
the size of single, levitated particles of known composition and at fixed temperatures and relative humidities may be monitored for prolonged times (of the order of days) to deduce evaporation rates.

There are several methods to measure the size of a levitated particle, e.g. direct imaging [4] or mass change monitoring by measuring the change in DC voltage to compensate gravitational force in an electrodynamic balance [5]. However, analyzing light scattering data using Lorenz-Mie theory is the method of choice to size dielectric microspheres. Measuring and analyzing the change in the angular scattering pattern (phase function) can be used to determine size and vapor pressure as demonstrated by Ray et al. [6].

Extremely high precision is achieved if one uses light scattering to measure cavity resonances in spherical droplets, a method called Mie resonance spectroscopy [50], [51].

Besides elastic light scattering these resonances have been detected also in fluorescence [9], Raman [10], [11] and infrared absorption spectroscopy [12].

For elastic light scattering typically a fixed wavelength laser source is used to measure light scattering intensity as a micron sized evaporating droplet passes through resonances [13]. This method of recording resonance spectra is working if the change in radius is monotonic, meaning in practice: sufficiently fast. It is not well suited for sizing low vapor pressure aqueous aerosol particles, because fluctuations in relative humidity and temperature lead to size changes, and hence to light scattering intensity fluctuations. For instance this will cause a particle to pass back and forward through a particular resonance several times, while its size slightly shrinks and rises because of the fluctuating relative humidity, a situation which makes the analysis impossible. Therefore, instead of a fixed wavelength source, inelastic scattering may be used [15], or a tunable light source may be employed to scan the resonance spectrum, as in the pioneering work of Ashkin and Diziedzic [50]. Refined procedures for measurement and analysis permit the determination of size and refractive index with a precision of $3 \times 10^{-5}$ [14].

Here we report an attractive and technically simple alternative approach, namely using a "white" light source with high spatial coherence to illuminate a levitated microdroplet and excite its resonance spectrum which is recorded by an optical multichannel analyzer.
3.3 Principles of the method

The extinction and scattering spectra of dielectric spheres with small absorption exhibit a ripple structure, i.e. irregular spaced sharp peaks as a function of the size parameter \( x = 2\pi r / \lambda \), with \( r \) being the radius of the sphere, and \( \lambda \) the wavelength [16]. These peaks are often called Morphology Dependent Resonances (MDRs) and can be interpreted as electromagnetic waves that, striking the surface of the sphere, are strongly confined within the particle by a series of almost total internal reflections and then focused on the surface in phase.

In Mie theory, the electromagnetic normal modes are resonant when the denominators of the scattering coefficients \( a_n \) and \( b_n \) in the infinite series expansion [16] are minima. For each index \( n \) there is a sequence of values of \( x \) for which the mode associated to \( a_n \) or \( b_n \) is excited. Following the convention introduced by Chýlek [17], we label the peaks with the type of mode (electric \( a_n \) or magnetic \( b_n \)), the index \( n \), and the sequential order number \( l \) of \( x \). The identification of an arbitrary mode of resonance in a measured spectrum, i.e. the unique determination of \( l \) and \( n \) and hence the correspondent size parameter and refractive index is possible but difficult because of the periodic recurrence of almost identical sets of resonance peaks [18].

However, the approximate determination of the particle size is possible without identification of the mode if the refractive index is known and \( \Delta x \) is measured; \( \Delta x \) being the size parameter spacing between consecutive resonance peaks in index number \( n \), \( \Delta x = x_{n+1}^l - x_n^l \), with the same order number \( l \). Under the assumption \( x \gg 1, x \sim n \) and \( mx \sim n, mx > n \), where \( m \) is the index of refraction, which holds when the broader resonance peaks are considered and the particle is larger than a few micrometers, the size parameter spacing becomes as in [17]:

\[
\Delta x = \frac{\arctan(m^2 - 1)^{1/2}}{(m^2 - 1)^{1/2}}.
\]  

(3.1)

The accuracy of this approximation has been evaluated to be better than 1% for \( |x - n| < 4 \) [19].

The wavelengths \( \lambda_{n+1}^l \) and \( \lambda_n^l \) associated with two consecutive modes of resonance can be determined directly from a resonance spectrum. The spacing \( \Delta x \) is derived from Eq. (3.1), where the refractive index can be interpolated from literature data if the composition of the particle is known [20]. This yields for the radius:

\[
r = \frac{\Delta x}{2\pi} \left( \frac{1}{\lambda_{n+1}^l} - \frac{1}{\lambda_n^l} \right). \]

(3.2)
If the radius and radius change of a particle is known, the vapor pressure can be calculated applying the evaporation equation, here in the form as in [1], rearranged from the original formulation given by Maxwell in 1877 [22]:

$$\frac{dr}{dt} = \frac{DM}{R \rho r} \left( \frac{p_\infty}{T_\infty} - \frac{p}{T} \right) \Phi,$$

(3.3)

where $r$ is the radius of the particle, $D$ the gas diffusivity of the constituent species with respect to ambient air, $M$ is the molecular weight, $\rho$ the density, $R$ the gas constant, $p$ and $p_\infty$ are the vapor pressures at the surface of the particle and at infinite distance.

The diffusivity $D$ is calculated through:

$$D = \frac{3\pi \sqrt{2}}{64} \left( \frac{1}{n_0 d_c^2} \right) \left( \frac{RT}{M} \right)^{\frac{3}{2}},$$

(3.4)

where $n_0$ is the number density concentration of the ambient air, and $d_c$ the collision diameter between a molecule of ambient air and a molecule evaporated from the particle [1].

We assume that the gas system is dilute enough to neglect the vapor pressure of the species at a large distance from the particle, hence $p_\infty = 0$. Also, the evaporation rate is very slow, because of low vapor pressure, that no detectable cooling due to evaporation at the particle surface occurs, so that $T_\infty = T$. For particles bigger than $1\mu m$, the correction term $\Phi$, calculated for instance by Fuchs [23] is $\Phi \cong 1$. These considerations simplify Eq. (3.3), and the vapor pressure can be expressed as follows:

$$p = r \frac{dr}{dt} \frac{RT \rho}{M D},$$

(3.5)

which implies that the quantity $rdr/dt = \frac{1}{2} dr^2/dt$ stays constant during the evaporation of a particle at constant temperature.

Thus, Eq. (3.5) can be conveniently reformulated as:

$$p = \frac{1}{2} \frac{dr^2}{dt} \frac{RT \rho}{M D}.$$  

(3.6)

The size change of an evaporating particle can be determined without identifying the exact mode by considering that it will be reflected in a shift of the resonance spectrum. If one tracks only the position of one arbitrary distinct mode of resonance during its shift, the index number $n$ and order number $l$ will remain of course constant, meaning that the resonance size parameter of the mode, $x_{mode}$, remains constant as well [15].
3.4 Experimental setup

This property allows the calculation of the radius at every time through the mere definition of the size parameter:

\[ r = \frac{x_{\text{mode}} \lambda_p}{2\pi} \]

where the size parameter is calculated at the beginning of the analysis knowing the location of the chosen peak in the spectrum, \( \lambda_p \), and the radius from Eq. (3.2). The vapor pressure follows now from the linear time evolution of \( r^2 \) and Eq. (3.6).

3.4 Experimental setup

The basic experimental setup has been described previously [24], [25]. Briefly, an electrically charged particle (typically 5-15 \( \mu \)m in radius) is levitated in an electrodynamic balance [26], see a schematic of the setup in Fig. 3.1. The balance is hosted within a three wall glass chamber with a cooling agent flowing between the inner walls and an insulation vacuum between the outer walls. A constant flow (typically 30 sccm) of a \( \text{N}_2/\text{H}_2\text{O} \) mixture with a controlled \( \text{H}_2\text{O} \) partial pressure is pumped continuously through the chamber at a constant total pressure adjustable between 200 and 1000 mbar. The temperature can be varied between 330 K and 160 K with a stability better than 0.1 K and an accuracy of \( \pm 0.5 \) K. Relative humidity (RH) in the chamber is set by adjusting the \( \text{N}_2/\text{H}_2\text{O} \) ratio, using automatic mass flow controllers.

During an experiment, the temperature and the relative humidity are kept constant while measuring a particular evaporation rate. The relative humidity is registered by a capacitive thin film sensor that is mounted in close vicinity of the levitated particle (<10 mm). The sensor was calibrated directly in the electrodynamic balance using the deliquescence relative humidity of different salts. Its accuracy is \( \pm 1.5\% \) RH between 10\% and 90\% RH.

A single-particle generator (Hewlett-Packard 51633A ink jet cartridge) is used to inject a liquid particle from solutions prepared by mass percent with MilliQ water using an analytical balance and analytical grade reagents with purities of 99\% or higher. Two collinear laser beams illuminate the particle from below (HeNe @ 633 nm, Ar\(^+\) @ 488 nm).

To size the particle three different, independent methods are employed. First, we use the video image of the particle on CCD detector 1 and an automatic feedback loop to adjust the DC-voltage for compensating the gravitational force [44]. A change in DC voltage is therefore a direct measure of the mass change, allowing to calculate a radius change when the density of the particle is known or can be estimated.
Spectrograph
OMA

Figure 3.1: Schematic of the apparatus. A three-wall glass chamber hosts four metal rings which supply the electric field needed for particle levitation. The particle is illuminated by two laser beams from below and by the LED from aside. The scattered light is collected in the near and far field view by two CCD cameras, and fed into a spectrograph via an optical fiber.

Second, the two-dimensional angular scattering pattern is recorded with CCD sensor 2 by measuring the elastically scattered light from both lasers over observation angles ranging from 78° to 101°. If the particle is liquid, and therefore of spherical shape the scattering pattern is regular, with the mean distance between fringes being a good measure of the radius of the particle, almost independent of its refractive index [28].

Third, we have added a ball lens type point source LED (EPIGAP GmbH, Germany) as a “white light” source with high spatial coherence (50 μm source diameter, peak wavelength ≈ 589 nm, spectral bandwidth at 50% ≈ 16 nm, radiant power ≈ 150 μW) using a bestform lens (f = 32 mm, f/μ = 2.0) to focus the light on the levitated particle and a pierced mirror to collect the Mie resonance spectra in a backscattering geometry (as shown in Fig. 3.1, collection angle 180°±4°).

Although resonance spectra may be measured in other scattering geometries, backscattering gives the advantage of using approximate solutions for calculating the resonance positions [18]. Two holographic notch filters are used to reject the elastically scattered light of both lasers and an optical fiber is employed to deliver the backscattered light from the particle to a 150 mm spectrograph with a slow scan backilluminated CCD array detector as an optical multichannel analyzer (OMA). The resolution of the
Figure 3.2: Example of the experimental dataset processing. Panel (a): The LED reference spectrum (red curve) and the original intensity of light scattered by the particle (aqueous malonic acid particle, radius ca. 8.1 μm, refractive index ca. 1.41, black curve). The latter is plotted in panel (b) after background correction and dividing by LED reference. The signal is smoothed by application of an FFT filter and shown in panel (c).

The spectrograph-OMA combination is about 0.5 nm; this excludes the observation of the narrowest resonances in the backscatter spectrum.

Figure 3.2 illustrates how a resonance spectrum is obtained with this setup. The red curve in panel (a) shows the intensity measured when the particle is removed from the illuminated region by applying an additional DC voltage to the endcaps of the electrodynamic balance. This is the emission spectrum of the LED originating from reflections from the walls of the chamber, which serves as reference in the following. The black line in panel (a) shows the backscattered intensity when the particle is moved back into the center of the balance. Dividing this spectrum by the reference leads to the spectrum of panel (b), which is further processed with a smoothing FFT filter employing the bandwidth of the spectrograph-OMA combination. The resulting Mie resonance spectrum is plotted in panel (c) of Fig. 3.2, showing the typical double-peak
structure.

To compare the proposed method for measuring evaporation rates with a fixed wavelength approach [13], we recorded the glare spot intensities measured with CCD 1 at a wavelength of 633 nm with a 1 Hz temporal resolution. A critical comparison of the two methods will be found in the next section.

3.5 Results and discussion

The setup described above has been used to determine the vapor pressure and the heat of vaporization of aqueous malonic acid. As an illustration, the temporal evolution of the experiment is depicted in Fig. 3.3. The uppermost panel displays the relative humidity and the balancing DC voltage proportional to the mass of the particle. The relative humidity, after an initial transient, is kept constant at 52%, then lowered to reach a constant value of 42% at 60 ks, and then decreased further to 33% at 122 ks, so that the particle experiences three long periods of constant relative humidity separated by fast changes during which it shrinks while adjusting to thermodynamic equilibrium. We focus our attention on the three periods with constant RH, where the shrinking is due to evaporation of malonic acid to the gas phase, and stress the fact that they correspond to three different concentrations of the aqueous solution particle, from a more dilute one at the beginning to a more concentrated one at the end. The concentrations, corresponding to the relative humidities mentioned above, were determined from literature data based on EDB measurements [29], and are 80%, 86% and 92% in weight respectively. These values are used for the calculation of the refractive index [20]. Together with spectra as that shown in Fig. 2, these values allow to deduce size parameter spacing and finally the radius through Eq. (3.2) and Eq. (3.7).

In panel (b) it is shown how the resonance spectra evolved during an experiment. A shift of the spectra in the regions of constant RH is evident. More, it is also clear from the slope that the shift is faster when the RH is lower, and hence the concentration of the particle is higher, meaning that a more concentrated particle is evaporating faster than a more dilute one.

A maximum located at 600 nm in the first spectrum is chosen and followed during its shift (panel (c) of Fig. 3.3). When its location exits the wavelength domain of our detection device at 100 ks a new peak is chosen at 580 nm and the tracking is continued.

Panel (d) shows the evolution of $r^2$ and its linear fits in the regions of constant relative
3.5. Results and discussion

Figure 3.3: Experimental raw data from a vapor pressure measurement of an aqueous malonic acid particle at 291 K exposed to different relative humidities. The uppermost panel (a) shows the DC voltage (proportional to the mass) necessary to compensate the gravitational force (black line). The red line is the relative humidity. Panel (b) shows the corresponding resonance spectra, with color-coded intensity. The values in the palette represent the intensity of the scattered light divided by the reference LED signal, as explained in the caption of Fig. 3.2. In panel (c) the location of the resonance peak at 600 nm at t=0 is tracked during its shift (gray line) up to t=100 ks, where it exits the domain of our spectrograph. Thus, a new peak at 592 nm and t=100 ks is chosen and tracked up to 190 ks. The corresponding $r^2$ is calculated through Eq. (3.7) and displayed in panel (d) together with the linear fits in the regions of constant RH (red green and orange overlapped lines). The results of the three fits are: $dr^2/dt = -3.81 \times 10^{-5} \mu m^2/s$, $-4.14 \times 10^{-5} \mu m^2/s$, and $-4.82 \times 10^{-5} \mu m^2/s$ for RH=51%, 42% and 32%.
Figure 3.4: Panel (a) shows 90'000 s (roughly 24 hours) of the same raw data already presented in Fig. 3; malonic acid particle at 291 K and 32 % relative humidity, size ca. 7.2 μm. Panel (b) shows for comparison the scattered intensity at the fixed wavelength of the HeNe laser (633 nm at 90° scattering angle, sampled with 1 Hz). Panel (c) and (d) show the same kind of data - also for a time span of 90'000 s - for a malonic acid particle at 273.5 K and 21% relative humidity, size ca. 6.3 μm.

humidity (colored lines) which yields the quantity $\frac{dr^2}{dt}$ necessary to obtain the vapor pressure from Eq. (3.6).

Let us briefly discuss the advantages of the proposed method for measuring evaporation rates by comparing it to the more conventional one using a fixed wavelength laser source to measure the temporal evolution of scattered light intensity as illustrated in Fig. 4. Panel (a) and (b) of Fig. 4 show raw data for a particle under conditions leading to a relatively high evaporation rate ($4.82 \times 10^{-5} \mu m^2/s$). It is obvious that both, the spectral shift of a resonance peak shown in panel (a) and the scattered light intensity with time as shown in panel (b) could be used to retrieve the evaporation rate here. Panels (c) and (d) show the data of a particle evaporating at a considerably lower rate ($5.09 \times 10^{-6} \mu m^2/s$). While under these conditions the resonance peak shift can be clearly evaluated this is no longer possible for the fixed wavelength data simply because there are not enough resonance peaks appearing in the data because of the small overall radius change within 24 hours. To make the method work the particle has to
3.5. Results and discussion

Figure 3.5: Vapor pressure of aqueous malonic acid measured at different temperatures as a function of concentration in mole fraction. All experimental points are fitted simultaneously to Eq. (3.8) (except for the datapoint at \( x = 0.12 \) at \( T = 291 \) K), leading to the corresponding colored lines. The shaded area represents the region of unreliability of our measurements (see text for a detailed description).

Shrink at least 3 size parameter units. Also, note that it becomes increasingly more difficult to interpret the type of data shown in panels (b) and (d) if there are fluctuations in relative humidity during the measurements leading to a non monotonous radius change. This could lead to passing through the same resonance back and forward several times at a fixed wavelength with no simple means to correct for this effect. The spectral shift data of a resonance peak in panels (a) and (c) become more noisy under such circumstances but still allowing to deduce rates if the distortion is not too severe. We conclude that the proposed method is about two orders of magnitude more sensitive in measuring low vapor pressures and considerably less sensitive to fluctuations in relative humidity compared to a fixed wavelength measuring approach.

To obtain the vapor pressure the diffusivity is needed. Since we are not aware of any experimental measurements of the diffusivity of malonic acid in nitrogen, it has been evaluated through Eq. (3.4) taking the value of the collision diameter given in Bilde et al. [30]. For the calculation of the diffusivity Bilde et al. followed Bird et al. [31] instead of using Eq. (3.4). The agreement between diffusivities using Eq. (3.4) and
those calculated in [30] is between 5% and 10% depending on the temperature.

The measurements are performed at constant RH, which means constant aqueous solution concentration. Therefore the evaporation of malonic acid is accompanied by an equal (in terms of molecules) evaporation of water to the gas phase. Thus, the vapor pressure calculated through Eq. (3.6), which holds for a one component system, has to be corrected by multiplying it by the molar fraction of the malonic acid concentration.

Figure 3.5 summarizes the results obtained from vapor pressure measurements of malonic acid at the investigated temperatures and humidity conditions.

Assuming a Clausius-Clapeyron relationship between vapor pressure and temperature, we can write the following equation:

\[
p = p_0 \gamma x \exp \left[ -\frac{\Delta H^\circ}{R} \left( \frac{1}{T} - \frac{1}{T^\circ} \right) \right],
\]

where \( p_0 \) is the vapor pressure of the pure substance under standard conditions, \( \gamma \) is the activity coefficient at each concentration calculated using the UNIFAC parametrization by Peng et al. [29], \( x \) is the concentration in mole fraction, \( \Delta H^\circ \) is the standard heat of vaporization.

In order to estimate the errors of the vapor pressure measurements let us consider first the pure substance under study (malonic acid). The resolution of the spectrograph is 0.5 nm at 585 nm, the size of the aerosol particle and its residence time in the electrodynamic balance are typically 8 \( \mu \)m and 100 ks. This leads to an uncertainty in the evaporation rate of \((dr^2/dt)_{\text{min}} = -1 \times 10^{-6} \mu \text{m}^2/\text{s}\), which corresponds through Eq. (3.5) to a minimum detectable vapor pressure and a constant error in vapor pressure of \(p_{\text{min}} = 1.25 \times 10^{-6} \text{ Pa}\). Moreover the radius of the particle calculated from Eq. (3.2) with an estimated maximal error of 5% propagates to a relative error in the vapor pressure of 30% through Eq. (3.5). These are the error bars shown in Fig. 3.5.

The extension to the mixed system malonic acid/water includes an additional contribution due to a possible drift in relative humidity. This will result in a particle radius change which is superimposed on the change due to evaporation of malonic acid to the gas phase. A mere 0.5% drift at 90% RH (molar fraction concentration \( x = 0.18 \)) will result in a 0.15 \( \mu \)m size change on a 8 \( \mu \)m particle. During an experiment running over 100 ks, this radius change corresponds to an apparent evaporation rate of \(dr^2/dt = -5.9 \times 10^{-5} \mu \text{m}^2/\text{s}\), and an apparent vapor pressure of \(1.1 \times 10^{-5} \text{ Pa}\). The same calculation repeated for different relative humidities leads to the upper contour of the shaded area in Fig. 3.5, where we cannot measure the vapor pressure reliably with our present relative humidity control. Also datapoints close to this area are to a
3.6. Conclusions

small degree affected, but it is not taken into account in the error bars shown in Fig. 3.5.

To see whether the estimation of the shaded area is correct we performed also experiments with highly diluted aqueous sulfuric acid particles at high relative humidities. Since aqueous sulfuric acid at low concentrations and room temperature has a sulfuric acid vapor pressure smaller than $10^{-13}$ Pa an apparent drift in the resonance spectra must be due to a drift in relative humidity. The drifts observed were consistent with the shaded area shown in Fig. 3.5.

A fit to Eq. (3.8) leads to a vaporization enthalpy $\Delta H^{\circ}$ of $100 \pm 17$ kJ/mol, a vapor pressure $p_0$ of $(3.2 \pm 1.2) \times 10^{-4}$ Pa at standard temperature $T^\circ = 298.15$ K for malonic acid as a supercooled melt, and a vapor pressure of the saturated aqueous solution of malonic acid (at $x = 0.22$) $p_{sat} = (4.1 \pm 1.6) \times 10^{-5}$ Pa at $T^\circ = 298.15$ K, corresponding to the vapor pressure of the crystalline solid.

These values compare with a $\Delta H^{\circ}$ of $92 \pm 15$ kJ/mol and a vapor pressure of $6.0 \times 10^{-4}$ Pa at 298.15 K measured for pure malonic acid with the TDMA technique [32]. The enthalpy agrees within the experimental errors and the vapor pressure comparison suggest that in the TDMA measurements the malonic acid was also present as a supercooled melt. Considering the relative error of about 35% of both vapor pressure measurements [32], the agreement is reasonable.

3.6 Conclusions

A new and simple experimental approach to Mie spectroscopy using a ball-lens LED as "white" light source and a simplified treatment of the Morphological Dependent Resonances have been presented and tested on an aqueous malonic acid micron sized particle, a dicarboxylic acid of interest for atmospheric science.

The size and the evaporation rates of the particle levitated in an electrodynamic balance have been measured for different ambient conditions of temperature and relative humidity. This method of recording resonance spectra works even if the change in radius is not monotonic, making it especially suited to study binary aqueous solution aerosol particles at elevated relative humidities. For example, it might be of use when determining binary activity coefficients [33].

As a useful application we calculated the enthalpy of vaporization and the vapor pressure of the malonic acid depending on concentration and temperature: $\Delta H^{\circ} = 100 \pm 17$ kJ/mol for the enthalpy of vaporization, $p_0 = (3.2 \pm 1.2) \times 10^{-4}$ Pa for the super-
cooled melt at a standard temperature of $T^\circ = 298.15$ K, and $p_{sat} = (4.1 \pm 1.6) \times 10^{-5}$ Pa for the vapor pressure of the saturated malonic acid solution particle.

We think that this alternative approach has potential to become a widespread simple and relatively cheap method for sizing spherical homogeneous levitated particles.

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Bibliography


3.7 A related paper

The author of this dissertation contributed and appear as co-author in the following paper, recently published [53]. I applied the optical technique described in the previous section to measure the vapor pressure of an oxalic acid aqueous aerosol particle. The results of these measurements contributed to develop a broader analysis of the role of oxalic acid as heterogeneous ice nucleus in the upper troposphere. Since the subject of the following paper, ice nucleation, is not a main concern for the work here presented, I decided to include only the abstract.
“Oxalic acid as a heterogeneous ice nucleus in the upper troposphere and its indirect aerosol effect”

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ATMOSPHERIC CHEMISTRY AND PHYSICS 6: 3115-3129 JUL 27 2006
3.7.1 Abstract

Heterogeneous ice freezing points of aqueous solutions containing various immersed solid dicarboxylic acids (oxalic, adipic, succinic, phthalic and fumaric) have been measured with a differential scanning calorimeter. The results show that only the dihydrate of oxalic acid (OAD) acts as a heterogeneous ice nucleus, with an increase in freezing temperature between 2 and 5K depending on solution composition. In several field campaigns, oxalic acid enriched particles have been detected in the upper troposphere with single particle aerosol mass spectrometry. Simulations with a microphysical box model indicate that the presence of OAD may reduce the ice particle number density in cirrus clouds by up to similar to 50% when compared to exclusively homogeneous cirrus formation without OAD. Using the ECHAM4 climate model we estimate the global net radiative effect caused by this heterogeneous freezing to result in a cooling as high as -0.3 Wm\(^{-2}\).
Chapter 4

Hygroscopic properties, H-TDMA measurements

This Chapter is about a paper to which the author of this dissertation contributed and appear as a co-author.
Hygroscopic growth and water uptake kinetics of two-phase aerosol particles consisting of ammonium sulfate, adipic and humic acid mixtures

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4.1. Abstract

The hygroscopic growth of solid aerosol particles consisting of mixtures of ammonium sulfate (AS) with either adipic acid (AA) or Aldrich humic acid sodium salt (NaHA) was characterized with a hygroscopicity tandem differential mobility analyzer (HTDMA) and an electrodynamic balance (EDB). In particular, the time required for the aerosol particle phase and the surrounding water vapor to reach equilibrium at high relative humidity (RH) was investigated. The pure substances studied have short equilibration times, <1s. However, depending on the mixing ratio of AS/AA, residence times of up to 40 seconds were required to reach equilibrium at 85%RH, yielding a measured hygroscopic growth factor up to 7% too low from measurements at 4 s residence time compared to measurements at equilibrium. We suggest that the solid AA, when present as the dominant component, encloses the water-soluble inorganic salt in veins and cavities between the AA crystals, resulting in the observed slow water uptake. The presence of the salt solution in veins would cause a negative curvature of the solution meniscus at the opening of the pore, resulting in an inverse Kelvin effect that enhances the water uptake. The 1:3 and less strongly the 1:2 AS/AA (mass ratio) mixtures tested did indeed show deviations from the water uptake predicted with the Zdanovskii-Stokes-Robinson relation (ZSR). The AS/NaHA mixture (1:3 mass ratio) studied showed lower hygroscopic growth than predicted by ZSR, as was also noted in previous work and was explained there with ion/molecular interactions between the AS and the NaHA. The growth at the shortest residence time investigated was 4% lower than the growth at equilibrium for this mixture. In conclusion, it is important for studies of mixtures of water soluble compounds with insoluble material to allow for sufficient residence time at the specified humidity to reach equilibrium before the hygroscopicity measurements.
4.2. Introduction

Aerosol particles in the atmosphere affect the earth’s radiation balance in various ways (IPCC, 2001). Firstly, aerosol particles absorb and scatter radiation. This direct aerosol effect is influenced by the hygroscopicity of the aerosol particles, which is determined mainly by their chemical composition. Secondly, the tendency for cloud formation and resulting cloud properties similarly depend on chemical composition, as well as on number and size distribution of the aerosol particles (Kreidenweis et al., 2005; McFiggans et al., 2005; Rissler et al., 2004). Thus the cloud albedo and radiative properties of cloud droplets are influenced by aerosol hygroscopicity, coined the indirect aerosol effect.

Atmospheric aerosol components can be classified into inorganic and organic components (e.g. Kanakidou et al., 2005). The hygroscopic properties of most inorganic salts present in the atmosphere are well known (e.g. Ansari & Pandis, 1999; Clegg, Brimblecombe & Wexler, 1998; Colberg, Luo, Wernli, Koop & Peter, 2003). Of the many organic species identified in the aerosol (e.g. Putaud et al., 2004; Rogge, Mazurek, Hildemann, Cass & Simoneit, 1993; Saxena & Hildemann, 1996), the hygroscopic properties of quite a few pure substances have been investigated. However, to date the hygroscopic properties of only a few mixtures have been investigated (e.g. Chan & Chan, 2003; Cruz & Pandis, 2000; Marcolli, Luo & Peter, 2004; Mikhailov, Vlasenko, Niessner & Pöschl, 2004; Wise, Surratt, Curtis, Shilling & Tolbert, 2003).

Inorganic salts (for instance ammonium sulfate (AS) and sodium chloride) can show a hysteresis behavior during uptake and loss of water, i.e. by exhibiting a difference between the deliquescent and efflorescent relative humidities (DRH/ERH), and with a higher water content of the deliquesced than the effloresced particles in this relative humidity (RH) range. Conversely, organic constituents of the aerosol without hysteresis behavior can contribute to an uptake of water at lower RH than the DRH of inorganic salts. This has been reported by Dick, Saxena & McMurry (2000) and Posfai et al. (1998) and is also theoretically
expected, as such complex mixtures can remain in the liquid state and exchange water with the gas phase at lower RH’s (Marcolli et al., 2004).

In order to characterize such phenomena, the hygroscopicity of aerosols is investigated. Furthermore, hygroscopicity data are also needed for parameterization of thermodynamic models (Topping, McFiggans & Coe, 2005a), which are also used for modeling physico-chemical properties of the atmosphere in global models (Martin, 2000).

The response of aerosol particles to changes in RH can be measured by a variety of instruments. The particle levitation technique using an electrodynamic balance (EDB) has been demonstrated to be a valuable method for studying the hygroscopic properties of single aerosol particles (Davis, Buehler & Ward, 1990; Tang, 1997). This technique has the advantage that the particle mass can be monitored continuously as a function of RH, thus providing unambiguous in situ and artifact free characterization of the particle mass growth due to water uptake. Disadvantages of the levitation technique are that it works only with relatively large particles with diameters of several micrometers and that the technique is not suited for a direct investigation of ambient particles. A different method for characterizing water uptake is the hygroscopicity tandem differential mobility analyzer (HTDMA, Liu et al., 1978; Rader & McMurry, 1986). In the field, hygroscopicity measurements are commonly performed by means of an HTDMA. This technique is being used at a number of sites all over the globe.

Mass transfer effects in hygroscopic measurements of aerosol particles have recently obtained more attention (Chan and Chan, 2005). It has been discussed whether organic/inorganic aerosol mixtures show diffusion limitations of water (contrary to pure inorganic salts which equilibrate very fast, within timescales of < 1 s). Studies of how the hygroscopicity is reduced by coatings have been performed (Andrews & Larson, 1993). Kerminen (1997) considered the gas-phase transfer to particles before cloud activation. A field study by Chuang (2003) found that a fraction of the particles exhibited a slower water uptake than the majority of particles sampled, which was explained by a low mass accommodation coefficient.
in that study. Chan et al. (2005) did a review of the different studies investigating mass transfer effects for water uptake of aerosol particles, concluding the need for further investigation. Cubison (2005) described the experimental set-up and results for several systems. This study further investigates and analyzes the results from measurements with varying residence times at elevated RH.

In this paper measurements performed by two HTDMAs are being compared with each other and with results obtained with an EDB. One of the HTDMAs is from the University of Manchester (UMan), UK (Cubison, Coe & Gysel, 2005), the other one from the Paul Scherrer Institute (PSI), Switzerland (Gysel, Weingartner & Baltensperger, 2002; Weingartner, Gysel & Baltensperger, 2002), while the EDB is from ETH Zurich (Colberg, Krieger & Peter, 2004). Hygroscopicity measurements for a variety of mixtures are presented, with the goal to supply more data for the literature. The growth of AS is compared with the theoretical prediction using the Aerosol Diameter-Dependent Equilibrium Model (ADDEM) (Topping et al., 2005a; Topping, McFiggans & Coe, 2005b) developed at the UMan. In the case of mixtures of different components (organic/AS), the hygroscopic growth was predicted using the Zdanovskii-Stokes-Robinson (ZSR) relation for water activities of mixed particles (Stokes & Robinson, 1966).

In order to evaluate the water vapor equilibration time, the residence time of the particles at high relative humidity was varied from seconds to minutes. AS was chosen as the representative inorganic salt in this study, as its hygroscopicity is well known and it is a common constituent in the atmosphere. Adipic acid (AA) was chosen as a model substance for an organic constituent. AA has a low vapor pressure and low hygroscopicity (as well as a high deliquescence relative humidity), and is only moderately soluble in water. At the RH's studied here it is present in its crystalline form, which is assumed to contribute to a prolonged water uptake equilibration time. It has also been identified in atmospheric samples (Kawamura & Sakaguchi, 1999; Kawamura, Semere, Imai, Fujii & Hayashi, 1996; Ray & McDow, 2005). Furthermore tests were carried out with the commercially available Aldrich humic acid sodium salt (NaHA). This compound serves as a proxy for humic-like substances that were identified as a major
component of the isolated organic matter in the atmospheric aerosol (Graber & Rudich, 2006; Kiss, Tombacz, Varga, Alsberg & Persson, 2003; Kiss, Varga, Galambos & Ganszky, 2002).

4.3. Experimental methods

Introduction of hygroscopic growth and the ZSR relation

The $GF$ of a particle at a certain relative humidity (RH) is defined as

$$GF(RH) = \frac{D(RH)}{D_0},$$

(1)

where $D_0$ is the dry particle mobility diameter measured at <10%RH, and $D(RH)$ is the mobility diameter at a specific RH. $GF$ indicates the relative size increase in mobility diameter of particles due to water uptake, and is presented in humidograms (i.e. showing the response in hygroscopic growth versus relative humidity, see Fig. 2). The hygroscopic growth factor of a mixture ($GF_{mixed}$) can be estimated from the growth factors of the pure components and their respective volume fractions, $\varepsilon$, with the ZSR relation (Gysel et al., 2004; Prenni, De Mott & Kreidenweis, 2003; Stokes et al., 1966)

$$GF_{mixed} = \left( \sum \varepsilon_i GF_i^3 \right)^{1/3},$$

(2)

where the summation goes over all compounds present in the particles. The model assumes spherical particles, ideal mixing behavior (i.e. no volume change upon mixing) and independent water uptake of the organic and inorganic components. Mobility growth factors obtained with an HTDMA are only equal to volume equivalent growth factors if the particles do not change the shape during water uptake. The volume fractions for the two components in the dry particles were calculated as
\[ e_i = \frac{(w_i / \rho_i)}{\sum_k (w_k / \rho_k)}, \]  

where \( w_i \) is the mass fraction and \( \rho_i \) the density of the pure substance \( i \). Values of \( \rho \) used in the model were 1.77, 1.36 and 1.1 g/cm\(^3\) for AS, AA and NaHA, respectively, obtained from the product suppliers. \((D/D_0)_{\text{org}}\) is the hygroscopic growth of AS, which was parameterized for the deliquesced state from our measurements, between 35-93%RH, with:

\[ GF = (1 - \%RH/100)^\gamma + c, \]  

where RH is given in percent, and the coefficients \( \gamma \) and \( c \) were fitted as -0.21821 and 0.070, respectively. The standard deviation of the residuals between this parameterization and the ADDEM model used was 0.012 in \( GF \) (Pruppacher & Klett, 1997; Seinfeld & Pandis, 1998; Topping et al., 2005a; Topping et al., 2005b).

**HTDMA**

The two HTDMAs employed (from UMan and PSI) are operated in a similar manner. A differential mobility analyzer (DMA1) selects a monodisperse aerosol size, \( D_\theta \), under dry conditions (RH<10%). The aerosol then passes through a humidifier with a controlled higher RH, and the diameter \( D \) is measured with a second DMA (DMA2). A scheme can be seen in Fig. 1. The instrument from PSI with a closed-loop sheath air uses only the aerosol flow entering the DMA2 to regulate the RH in the DMA2 (Weingartner et al., 2002). The RH of the sheath air thus follows the RH of the aerosol flow. RH setpoint changes were kept small, in order to maintain similar RH in the aerosol flow as in the sheath air. In this study data was used only if the difference in the sheath air was <1%RH during each individual scan. The two DMAs are similar to the TSI 3071 type.

The UMan instrument (Cubison et al., 2005) humidifies the aerosol flow and the sheath air flow with two independent humidifiers and controllers. The RH of the aerosol and the sheath air was kept similar for high accuracy measurements. The
Fig. 1: Experimental set-up of the HTDMA.

Two DMAs used were constructed in house and are of the Vienna design (Winklmayr, Reischl, Lindner & Berner, 1991).

Both HTDMAs were kept at a constant temperature set in the range 18-23 °C (controlled by a water bath). A few degrees cooling of DMA2 with respect to the aerosol and sheath air conditioners (at constant laboratory temperature) was necessary to reach high RH's (>90%RH). The relevant RH in DMA2 was determined by measurement of the system temperature and the DMA2 excess sheath air dew point using a dew point mirror. The accuracy of the RH measurement at higher RH is for example 90±1.2%, assuming no temperature gradients in the DMA2. The hygroscopic growth factor (GF) can be determined with a precision (2x standard deviation) of ∆GF ≈ ±0.01 (at D0) and ∆GF ≈ ±0.03 (at DRH). This is the largest spread in precision observed for the inorganic/organic mixtures, where changes in the geometrical shape factor presumably contribute to this spread. Measurements of solid inert material, such as mineral dust, performed with the same HTDMA set-up show a precision of ∆GF ≈ ±0.005 (see for example Vlasenko et al. (2005)).

Two different ways to operate the HTDMA were used; these are denoted hydration and dehydration mode. For the hydration mode, the mono-modal dry particles were exposed to a monotonously increasing RH until the size measurement in DMA2. For the dehydration mode the particles were first deliquesced at RH>80% in a pre-humidifier, and then the RH was monotonously lowered to the RH in DMA2, thus allowing the efflorescence relative humidity to
be measured. For the ERH measurements the DMA2 was kept at a temperature similar to the laboratory temperature in order to guarantee that the lowest RH behind the pre-humidifier occurs in DMA2, to avoid efflorescence before DMA2. The pre-humidifier switched on/off automatically. This setup allows a completely automated operation of the HTDMA (with only exchange of silicagel used for drying when needed).

Residence time chambers

In order to study the effect of residence time of the aerosol in the HTDMAs, 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. The chambers were kept at the same temperature as the DMA2 in order to ensure constant RH from the chambers to DMA2. The chambers were of different sizes yielding residence times ($\tau_{\text{res}}$) ranging from 3 s to 2 min in total. The errors in the calculation of $\tau_{\text{res}}$ are the sum of the uncertainty in measurements of geometry and of the uncertainty in the measured residence time (approximated as the width of sigmoidal step change, see below). The total errors were thus on the order of $\pm 4$ s for $\tau_{\text{res}} < 30$ s and $\pm 11$ s for $\tau_{\text{res}} > 30$ s. The geometries of the chambers were chosen as cylinders with a ratio of length to diameter of about 3 to 10, because of space availability and construction reasons. The response time from the chamber entry to the chamber exit (at entry to DMA2) was measured. The residence time for the chambers was chosen as the 50% value of the step change on the resulting sigmoidal curve. As some mixing occurs in the chambers the sigmoidal curves become stretched out over 21 s (for a signal response from 10 to 90%) for the largest chambers, with $\tau_{\text{res}} \geq 30$ s. However, several measurement scans, each with a duration varying between 1-3 min, were done after switching to the chamber with the longest $\tau_{\text{res}}$ to allow for a steady state to build up. Then monotonously shorter $\tau_{\text{res}}$ were measured (by turning 3-way valves), until only connecting tubing was used for the shortest $\tau_{\text{res}}$. If the pre-humidifier was used, the $\tau_{\text{res}}$ was increased by 10 s (time from the middle of the pre-humidifier to the main humidifier). The residence times stated below are thus
from the middle of the first humidifier (pre-humidifier or main humidifier) through the tubing and residence chambers up to the entry point of the sheath air inside the DMA2. The time from the entry point of DMA2 to where the aerosol flow mixes with the sheath air is 3.5 s for the PSI HTDMA and 2 s for the UMan HTDMA.

**Electrodynamic balance**

An electrically charged particle (typically 2-10 μm in radius) is levitated in an electrodynamic balance (Davis et al., 1990). The RH is set by adjusting the N₂/H₂O ratio of constant gas flow, using automatic mass flow controllers. During an experiment, the temperature is kept constant while the RH is changed with a constant rate. The sensor was calibrated directly in the trap using the deliquescence relative humidity of different salts. Its accuracy is ±1.5%RH between 10%RH and 80%RH and ±3%RH above 80%RH.

To characterize the particle a HeNe laser (633 nm) illuminates the particle from below. The video image of the particle on a CCD detector and an automatic feedback loop are used to adjust the DC-voltage for compensating the gravitational force (Richardson, 1990). A change in DC voltage is therefore a direct measure of the mass change. If the voltage at dry conditions (RH<10%) corresponds to the dry mass of the particle \(M(dry)\) we can deduce the mass growth factor as shown in Fig. 2. In addition, we use a photomultiplier with a conical detection angle (approximately 0.2° half-angle) to measure the scattering intensity at 90° to the incident beam and feed this signal to an analog lock-in amplifier to measure the intensity fluctuations, that is, the root mean square deviation from the intensity mean (RMSD intensity). Because of its symmetry, a homogeneous spherical particle will show a constant scattering intensity and hence a very small fluctuation amplitude (corresponding to value of 0.04, for our noise level). A nonspherical particle will scatter light with different intensity in the detection angle depending on its orientation relative to the incoming laser beam. All particles perform Brownian rotational motion in an EDB, which leads to an RMSD intensity between 0.5 to 5 depending on the deviation from spherical
symmetry of the particle in its dry, solid state. We have used these intensity fluctuation amplitudes previously to characterize liquid microdroplets with a single solid inclusion (Braun & Krieger, 2001; Krieger & Braun, 2001). In the following we will use this to identify the occurrence of phase transitions and to characterize the morphology of complex aerosol particles.

**Aerosol generation / substances tested**

Aerosol mixtures were generated using an atomizer (Type TSI 3076) operated with compressed air, purified with high efficiency particulate air (HEPA) filters followed by a carbon unit. Details on the substances investigated are found in Table 1 below. The substances were dissolved in MilliQ-water (18 MΩ-cm). All solutions appeared completely dissolved at visual inspection. It is assumed that the resulting aerosol was an internal mixture with the same mass ratio as in the solution, (cf. Gysel et al., 2004). This seems plausible, as no broadening of the growth factor distributions from the HTDMA could be detected while switching from the pure AS to the mixtures. The solutions were diluted further with MilliQ-water in the case the original solution yielded too high particle concentrations for the HTDMA at the size studied. The nebulized aerosol produced was subsequently dried in a silica gel diffusion dryer (residence time 30s) and the dried particles were neutralized by means of a Kr-85 source and then fed into the HTDMA for the hygroscopicity measurement.

**4.4. Results**

**Comparison of the two HTDMAs with pure AS**

The sizing of the DMAs in both instruments was verified with polystyrene latex spheres in the size range from 90-400 nm. Thereafter instrument performance was verified by measurements of hygroscopicity of the ammonium sulfate (AS). AS is a well investigated substance and the two HTDMA instruments measured reproducible results \( GF_{PSI} = 1.48 \) and \( GF_{UMan} = 1.46 \) at 80%RH and for
Fig. 2: Humidogram of laboratory-generated $D_0=100$ nm ammonium sulfate aerosol from the two HTDMAs (T $\sim$20°C). The two instruments show a good agreement.

Table 1: Substances used during the experiments

<table>
<thead>
<tr>
<th>Substance</th>
<th>Purity</th>
<th>Producer</th>
<th>Product n°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium sulfate, MicroSelect</td>
<td>99.5</td>
<td>Fluka</td>
<td>09978</td>
</tr>
<tr>
<td>Adipic acid, Puriss</td>
<td>99.6</td>
<td>Riedel-deHaen</td>
<td>27635</td>
</tr>
<tr>
<td>Humic acid, sodium salt, tech.</td>
<td>N.a.</td>
<td>Aldrich</td>
<td>H16752</td>
</tr>
<tr>
<td>isolated from crude lignite</td>
<td></td>
<td></td>
<td>(purchased 2003)</td>
</tr>
</tbody>
</table>
$D_v$=100 nm) which correspond well with literature (Hennig, Massling, Brechtel & Wiedensohler, 2005; Onasch et al., 1999). The modeled curve is calculated as in Topping et al. (2005a). The calculated DRH of AS is 79.9%RH for larger particles (Tang 1993) and 80.8%RH for diameter 100 nm particles, due to the Kelvin effect. The residence time ($\tau_{res}$) at the conditioned RH for different runs was varied between 4 and 40 s, and no influence of varying the $\tau_{res}$ was detected. This confirms that equilibration of inorganic salts is fast, $<<$ 1s (Chan et al., 2005; Kerminen, 1997). Measurements of AS were done at the beginning of the intercomparison period and after regular intervals (about every 2 weeks) thereafter.

Hygroscopicity of pure adipic acid and pure humic acid

Pure adipic acid (AA) does not show any uptake of water (e.g. $GF = 1.00 \pm 0.02$ up to 96%RH) (Hämeri, Charlson & Hansson, 2002; Joutsensaari, Vaattovaara, Vesterinen, Hämeri & Laaksonen, 2001; Prenni et al., 2001), which was confirmed up to RH 92% with both HTDMAs and the EDB in this study. AA is considered to be present as a crystalline solid which neither deliquesce in the range of mixtures used nor deliquesce for the humidities tested in this study. This was confirmed with the two-dimensional angular scattering pattern from the EDB.

The hygroscopicity of pure NaHA has also been measured in two former studies (Badger et al., 2006; Gysel et al., 2004). Within experimental error, our results on the growth of the deliquesced particles are comparable with these studies. However, measurements of the effloresced branch (hydration case) differ at lower RH just outside the experimental error. This could be due to different morphology of the particles caused by differences in nebuliser conditions and/or drying conditions after the nebuliser in the studies. Particles composed of only NaHA showed no difference in $GF$ as the residence time was varied at high RH. However, as the hygroscopicity of the NaHA is relatively low, the resolution of the HTDMA might not be sufficient to discern an effect for pure NaHA.
Hygroscopicity of AS/AA mixtures

The hygroscopic growth of 4 mixtures, with mass ratios of 1:1, 1:2, 1:3 and 1:4 AS/AA, were measured. In order to evaluate the equilibration time of the water uptake, the hygroscopic growth factor was measured with the HTDMAs at various residence times. The hygroscopic growth factors of deliquesced particles measured in the RH range 70-95% (for the hydration mode data only above DRH was used) were interpolated with an empirical fit to 85%RH for each mixture and residence time. Most points were measured in the vicinity of 85%RH. Fig. 3 shows box plots of the determined growth factors at 85%RH as a function of residence time for the 1:1, 1:2, 1:3 and 1:4 mixtures. The box plots consist of the mean growth factor (star), as well as 75/25 percentile (box) and 95/5 percentile (whiskers) of the residuals between the measurements and the fit line. Experimental uncertainties for the GF precision and $\tau_{res}$ accuracy are as stated in section 4.3.3.

Fig. 4 (EDB) and 5 (HTDMA) show the humidograms of the AS/AA mixtures for residence times sufficiently long such that the equilibrium size is reached. In the ZSR relation AA was assumed solid, thus not contributing to the growth at all ($GF=1.0$ at any RH). The presence of AA as a solid was confirmed by intensity fluctuation data from EDB measurements shown in Fig. 4: all mixtures over the whole relative humidity range show RMSD of scattered light intensity significantly above what is observed for completely liquid particles. Hence there was always a solid phase present in the particle. Note however, that at RH substantially lower than the DRH of ammonium sulfate the intensity fluctuations decrease as a consequence of water uptake, leading to an optically more homogeneous spherical particle. The water uptake below ammonium sulfate DRH is clearly detected by the hygroscopic mass growth. At DRH of AS the intensity fluctuations stay constant or increase again (1:1 and 1:2 mixtures) because the water content is now large enough for Brownian motion of the solid adipic acid inclusion in the aqueous solution particle to occur. There is a substantial deviation
Fig. 3: Hygroscopic growth for AS/AA mass ratio 1:1, 1:2, 1:3 and 1:4 (top to bottom panel), measured with different residence times. Dry particle diameter is 100 nm and GF relates to 85%RH. The 3s and 60s residence time data for the AS/AA 1:3 mixture was measured with the UMan HTDMA, rest of data was measured with the PSI HTDMA. Each box represents on average 44 data points.
Fig. 4: Experimental hygroscopic mass growth ($M/M_0$, solid lines in lower panels) and ZSR model (dashed lines in lower panels) and intensity fluctuation data (RMSD intensity, upper panels) from EDB measurements for three mixtures of AS/AA: (a) 1:1 in mass ratio, (b) 1:2, (c) 1:3. The shaded area labeled (S) marks the RMSD intensities typical for a solid non-spherical particle, the line labeled (L) marks the RMSD intensity for a completely liquid and hence spherical particle. See text for details.

of hygroscopic growth factors from ZSR prediction at RH above the DRH of ammonium sulfate for 1:2 and 1:3 mixtures, and a clear shift in DRH to lower RH for the 1:3 mixture. In 25 experiments with different particles of the 1:3 composition in the EDB we observed a scatter of values ranging from 1.16 to 1.45 in \( GF \) at DRH and a scatter ranging from 78 to 83%RH in DRH, which is significantly more scatter than instrument accuracy. This complex behavior of water uptake is most likely due to the morphology of the solid adipic acid (uptake in confined spaces, e.g. grain boundaries), and it will be discussed to some extent in section 4.3.5 and in more detail in a separate paper.

For the 1:1 AS/AA mixture, no increase in growth with longer residence time at high RH was noted for the interval studied here (4.4-40s), as can be seen from the top panel of Fig. 3. The hygroscopic growth of the 1:1 mixture is in good agreement with the ZSR approach (Fig. 4a and 5a) and with previous
Fig. 5: Humidograms of ammonium sulfate-adipic acid mixtures AS/AA. Mass ratios are indicated by the labels A-D, dry particle diameter is 100 nm and data points were measured at equilibrium (data for AS/AA 1:4 at residence time >30 s, see text).

measurements (Hämeri et al., 2002; Prenni et al., 2003). We did not observe a difference in growth with longer residence time for the 1:2 AS/AA mixture (Fig. 3).

In the HTDMA measurements of the 1:3 mixture, a dependence on residence time of the measured $GF$ was observed, which was larger than the experimental precision (estimated as 2x standard deviation), irrespective of the HTDMA instrument used (UMan or PSI). During the observable residence times (3 – 120 s) the $GF$ increased from 1.15 to 1.24, reaching its equilibrium value after about 10
s. For this mixture, the equilibrium hygroscopic growth exceeds the one predicted by the ZSR model by 0.08. This deviation is larger than the precision of the measurements, and also slightly larger than the typical deviations stated for instance in (Prenni et al., 2003), where the difference between measurement and prediction was on average 0.05 for 1:1 mixtures of ammonium sulfate and dicarboxylic acids at 90%RH. The 1:3 AS/AA mixture was also measured by (Hämeri et al., 2002) who reported a hygroscopic growth in agreement with ZSR predictions up to about 85%RH, but at higher RH the measured growth was higher than ZSR (i.e. GF 1.3 at 90%RH).

For the 1:4 mixture the hygroscopic growth doubles when the residence time is increased from 6 s to 40 s. A comparison with the ZSR model in Fig. 5d shows that the observed growth is below the predicted one, indicating that even 40 s may not be sufficient to reach equilibrium. Furthermore the irregularity of the particles increases with increasing AA content (see section 4.3.5), and we cannot exclude a compactation as the particles take up water, potentially leading to mobility diameter growth factors smaller than volume equivalent diameter growth factors due to significant shape effects in this case.

**Hygroscopicity of AS/NaHA mixture**

The hygroscopicity and dependence of residence time on the water uptake was measured for an AS/NaHA mixture with mass ratio 1:3 with the HTDMA. For this mixture a small increase, 0.04 in GF, was seen as the \( \tau_{res} \) increased from 10 s to above 30 s (Fig. 6). This is close to the limits of the experimental repeatability, but as the 95/5 percentiles for this mixture are quite small, we find it worth mentioning. This would imply that some mass transfer limitations can also be expected in the presence of NaHA, which is an amorphous solid. In section 4.3.5 (below), possibilities for mechanisms are discussed, which are based on two-phase systems. We investigated visually a mixture with a 1:3 mass ratio in a vial (~1 g total dry products), with water added accordingly to the measured hygroscopicity at 85%RH, and found the resulting mixture to be a thick paste,
with undissolved grains from the NaHA inside. Thus it seems probable that the less soluble fraction of the NaHA remains solid also at higher RH.

In Fig. 7 humidograms of the mixture and of pure NaHA can be seen. The results correspond well with other studies (Badger et al., 2006; Gysel et al., 2004). For the ZSR model, full efflorescence of AS at 35 %RH was assumed. The hygroscopicity of the mixture is low compared to the ZSR relation (panel A), which is explained by Badger et al. (2006) as interactions between AS and NaHA. They investigated a range of concentrations, which we refer to for further information.

Fig. 6: Hygroscopic growth for AS/NaHA mass ratio 1:3, measured with different residence times. Dry particle diameter is 100 nm and $GF$ relates to 85%RH. Data is from the UMan HTDMA, except the 29 s data which was measured by the PSI HTDMA.
Fig. 7: Humidogram of ammonium sulfate-humic acid mixture (NaHA) from PSI HTDMA, mass ratio 1:3 (A), as well as pure NaHA (B). Dry particle diameter 100 nm, data points measured at equilibrium.

4.5. Discussion on mass transfer and hygroscopicity

There are several possible reasons for the observed effect of prolonged water vapor equilibration times. This will be addressed in the following.

Mass transfer limitations of water vapor transport to the particle

If we consider a particle and the surrounding water vapor, the first limiting step could be the gas diffusion of water molecules to the particle’s surface (see e.g. Kerminen, 1997; Seinfeld et al., 1998). These studies show that gas diffusion is fast (i.e. <<1s), for the conditions used here. A subsequent step is the transfer across the gas-particle interface. This step is seen as a thin layer where water molecules are arriving from the gas, molecules are leaving the surface back to the gas, and molecules are diffusing into the particle. The rate governing these processes is described by the accommodation coefficient, α, defined as
\[ \alpha = \frac{\text{number of molecules entering the liquid phase}}{\text{number of molecular collisions with the surface}} \]  

(5)

Under the assumptions of a spherical particle, a constant water vapor pressure, an equilibrium governed by Henry’s law and a high water solubility, the accommodation coefficient, \( \alpha \), can be approximated with the following equation (Kumar, 1989):

\[ \alpha \geq \frac{R_p H_A \sqrt{2\pi M_A RT}}{3 \tau_p} \]  

(6)

where \( R_p \) is the particle radius, \( H_A \) the Henry’s law constant for water in the concentrated solution, \( M_A \) the molecular weight of water and \( \tau_p \) the time needed to obtain equilibrium. \( R \) and \( T \) are the universal gas constant and the temperature, respectively. If we consider the 1:3 mass ratio AS/AA mixture (measurements discussed in detail above), we obtained \( \tau_p = 10 \) s for a particle with diameter 100 nm, for which \( \alpha \) becomes \( >3 \times 10^{-6} \) (for \( H_A = 2.9 \text{ M} \cdot \text{g}^{-1} \cdot \text{atm}^{-1} \)). Such a low mass accommodation coefficient for a liquid in contact with the gas phase is not to be expected (Chuang, 2003; Schwartz, 1988; Seinfeld et al., 1998), thus the mass transfer is consequently assumed to be limited inside the particle. However, we cannot exclude that a fraction of the observed equilibration time stems from a slow uptake of water molecules into the particle across the predominantly organic surface, especially as long as the surface is dry.

If the particle is completely liquid the liquid diffusion should be fast (\( <<1 \) s for a submicrometer-sized particle consisting of a typical salt solution, if assuming a typical aqueous diffusion coefficient of \( 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1} \) (Seinfeld et al., 1998)). In the next section mass transfer limitations due to inhomogeneous morphology inside the particle will be discussed.
Influence of morphology on hygroscopic growth and transfer limitations

The hygroscopic growth of the AS/AA mixtures presented in section 4.3.4 shows deviations from the ZSR approach: for the HTDMA and the EDB measurements, the measured hygroscopic growths of the 1:3 and to a lesser extent the 1:2 mixtures are higher than predicted by the model with deviations that exceed the measurement uncertainties. Systematic changes of particle composition during the nebulizing process in the HTDMA or during the injection of a particle in the electrodynamic balance seem unlikely since such an effect was not found for other particle compositions. Moreover, we verified that no AA evaporated in the HTDMA by nebulizing pure AA particles for which no change in the mobility diameter was noted during the time in the HTDMA. This is consistent with the electrodynamic balance experiments which showed no weight loss of the particles over extended measurement periods.

The ZSR approach usually leads to accurate predictions of the water uptake of ammonium sulfate mixed with dicarboxylic acid mixtures (Choi & Chan, 2002; Marcolli et al., 2004). Since AA deliquesces only at 99.9%RH, we based the ZSR calculation for AS/AA mixtures on the assumption that there is no water uptake connected with the adipic acid fraction over the whole RH range. In addition to the results from the EDB as detailed above, we validated this assumption by determining the eutonic composition and the water activity of AS/AA mixtures by the methods described in Marcolli et al., (2004). The results in Table 2 show that the solubility of AA is reduced by about a factor of ten, while the one of ammonium sulfate remains unchanged within the error of the experiment. The water activity of the saturated AA solution is close to 1 while the eutonic composition deliquesces at a similar RH as AS. Moreover, we performed water activity measurements for 1:3 AS/AA aqueous suspensions in the range of $a_w = 0.8 - 1$ which showed good agreement with the ZSR model, indicating that the change of water activity due to the presence of dissolved or crystalline (particle sizes of a few micrometers) AA is below the detection limit. These bulk
measurements confirm the findings from the electrodynamic balance that AA remains crystalline over the whole measured humidity range.

In the following, we explore the possibility that the high water uptake of the 1:2 and 1:3 and the low one of the 1:4 AS/AA mixtures are due to morphological effects. SEM images were taken (Fig. 8) showing that under dry conditions, the AS/AA mixed particles consist of a conglomerate of nanocrystals with irregular shapes and diameters of 20–100 nm. When the DRH of ammonium sulfate is reached, it can be assumed that pores and veins between the crystals fill with aqueous ammonium sulfate. Due to capillary forces, the water uptake in such pores and veins is enhanced compared to the one of a flat surface. The enhancement depends on the vein diameter determining the concavity of the liquid surface and results in a Kelvin effect that is inverse compared to a convex liquid droplet. The inverse Kelvin effect can still be described by the standard Kelvin equation, while here the water activity has to be divided by the Kelvin factor to obtain the equilibrium RH (Eq. 7). To explore the influence of this effect, we have calculated the water uptake for a 1:3 AS/AA particle with vein systems of varying lengths. Assuming that the liquid portion of the particle is present totally in veins and keeping the length of the vein system constant with increasing RH, the veins have to increase in diameter to accommodate the increasing solution volume (for a schematic drawing, see Fig. 9). Thus, for a fixed length of the vein system and any given solution volume, the solution concentration (i.e. the Raoult effect) as well as the vein diameter assuming veins with circular cross sections (i.e. the Kelvin effect) is given and the equilibrium RH above the vein can be calculated by

$$RH = a_w \cdot e^{-4\sigma_{sol}\bar{V}_w\cos\phi/D_vRT}$$

In this equation $a_w$ is the water activity calculated from the growth factor of a pure AS particle as parameterized in Eq. 4, $\sigma_{sol}$ is the surface tension of the solution, $\bar{V}_w$ the partial molar volume of water, $D_v$ the vein diameter, $\phi$ the contact angle
Fig. 8: SEM images of spherical pure ammonium sulfate particles, irregular particles of the 1:3 ammonium sulfate/adipic acid mixture and pure adipic acid (from left to right). The dark spherical features in the pure AA frame are the holes of the Nuclepore filter and not deposited particles.

between the solution and the vein surface, $R$ the ideal gas constant and $T$ the absolute temperature. For simplicity, we calculated the vein diameter $D_v$ assuming that AS is totally dissolved and AA totally insoluble and approximated the surface tension of the solution by the one of water. Moreover, we assumed that the solution is completely wetting the vein surface ($\phi = 0^\circ$). This assumption is in accordance with Raymond and Pandis (2002).

In Fig. 10 the water uptake for a 100 nm diameter 1:3 AS/AA particle with a vein system of a total length of 400 nm is compared to the HTDMA measurement. This vein system length is compatible with a particle consisting of about eight AA crystallites with ~50 nm diameters. The inverse Kelvin effect leads to an enhanced water uptake above 50%RH. From 50 – 90%RH the vein diameter increases from 26 to 50 nm. These diameters have to be considered as upper limits, since in our model description, we assume that all the liquid is present in veins. In reality, it
will be present in grain boundaries, triple junctions as well as veins, resulting in smaller vein diameters for the same water uptake. We assume that above a critical upper value of RH the solution volume can no longer be accommodated within the veins and the inverse Kelvin effect vanishes. This upper limit does not seem to be reached yet for the 1:3 mixture, while in the case of the 1:2 mixture the slightly increased water uptake around 80%RH might indicate an inverse Kelvin effect which vanishes again at higher RH. An inverse Kelvin effect has also been postulated to explain a decrease in mobility diameter of soot and diiodomethane particles after exposure to water vapor (Jimenez et al., 2003; Weingartner, Burtscher & Baltensperger, 1997).

The inverse Kelvin effect also leads to a decrease of the DRH. For the vein system of a total length of 400 nm, a decrease of the DRH from 80.8 to 76%RH is expected. A slight decrease of DRH was observed for the particle in the electrodynamic balance, and a DRH of 78.8%RH was measured with the HTDMA for the AS/AA 1:3 mixture. We assume that after efflorescence the AS crystals are present in the veins or even totally enclosed by AA (see Fig. 9).
Fig. 10: HTDMA measurements of the 1:3 AS/AA mixture (dehydration mode) together with the water uptake modeled with the ZSR relation, as well as modeled with the additional water uptake of an inverse Kelvin effect from a 400 nm length vein system.

To capillary forces, water can enter the veins and dissolve AS partly before the deliquescence RH is reached, as can be seen from the mass increase of the particles in the electrodynamic balance starting at 50%RH. This partial dissolution is limited by the space available in the vein system and might be accompanied by a transport of AS out of the veins where it recrystallizes because the inverse Kelvin effect is no longer present. We assume that before the veins can start to grow in diameter, they have to be filled completely with solution because adhesion forces between crystals impede the expansion. Full deliquescence would therefore in this case only be reached at an RH closer to the one in the absence of a Kelvin effect.

We think that the long residence times needed in the HTDMA to reach full hygroscopic growth is due to the presence of AS in veins or even totally enclosed by AA. While the spreading of the solution in the veins should not be slowed
down considerably as long as the solution is wetting the vein surface (Liu, Wang, Wu & Zhang, 2005), the expansion of the veins in diameter might be the rate limiting step. Alternatively, in the case of a total enclosure, the AA forms a barrier that has to be overcome by the water molecules leading to a slow humidification. This effect seems to be stronger the higher the AA fraction is. The characteristic time for diffusion through the solid organic matrix can be described with (see e.g. Seinfeld & Pandis, 1998):

$$\tau_p = \frac{R_p^2}{\pi^2 D_{Sol}}$$

(8)

where $R_p$ is the particle radius, $D_{Sol}$ the solid diffusion coefficient and $\tau_p$ the characteristic time needed to reach equilibrium. If we calculate $D_{Sol}$, again for a 100-nm diameter particle and $\tau_p = 10$ s, we obtain $8.0 \cdot 10^{-13}$ cm$^2$ s$^{-1}$. This is a value in the range for solids, but would in our case only be applicable to a part of the particle. Thus under the assumption that a part of the particle remains effloresced, and water must diffuse through this solid matrix to dissolve the AS into ions that participate in the hygroscopic growth, a fraction of the equilibration times measured can be explained.

4.6. Conclusions

Some of the inorganic/organic mixed-phase solutions studied with an HTDMA in the present work required residence times up to 40 seconds in order for the particles to reach equilibrium after water uptake. It is proposed that the organic fraction, when present in major fractions, is solid and encapsulates some of the inorganic species residing in between the solid organic grains in veins and/or pores. The water uptake rate of the mainly inorganic solution is possibly slowed down by solid phase diffusion. It is important for measurements of such mixtures to allow for a sufficient residence time at the specified humidity for the system to equilibrate. Otherwise, the resulting underestimation of the hygroscopicity may
have implications for derived aerosol properties such as light scattering (direct aerosol effect in climate considerations) and cloud activation (indirect aerosol effect).

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References


Putaud, J. P., Raes, F., Van Dingenen, R., Bruggemann, E., Facchini, M. C., Deecesari, S., Fuzzi, S., Gehrig, R., Huglin, C., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N., Mulller,


In this chapter the hygroscopicity of two organic acids of atmospheric importance, citric acid (CA) and adipic acid (AA), as well as mixed together with an inorganic salt, ammonium sulfate (AS), will be presented. Ammonium sulfate is one of the most abundant inorganic constituent found in aerosol particles [40] [1]. Adipic and citric acids have been chosen for their very different hygroscopic behavior, i.e. a low and a high solubility, respectively. The technique for the characterization of an aerosol particle using an electrodynamic balance (EDB) together with the study of its hygroscopic properties can be found in Chapter 2.

5.1 Preliminary data analysis

The well described behavior of AS shown in Chapter 2 and Chapter 4 gets highly modified with a low degree of reproducibility by the presence of organic acids (see also Chapter 4). Some technical anomalies, probably related to the use of organics, complicated the interpretation of the data. For instance, Fig. 5.1 shows the time evolution of a slow hygroscopicity cycle of an AS+AA particle. The RH spans from very low values to high values and back with long periods in which it is kept constant or slowly varying. A drift in the voltage signal (proportional to the mass to charge ratio) in regions of constant RH is evident from the left graph in Fig. 5.2. This did not happen for pure AS (see Fig. 2.5) or even for other mixtures of AS and organic acids, like the one with glutaric acid described in Appendix B. The drift is then much higher than the one which could be due to a slow water uptake of AS (the AA does
not take up any water). Thus, any mass transfer limitation due to the presence of organic material on the surface of the particle can be excluded. This is also clear from the fact that a negative drift should eventually be present in regions of RH decrease. Instead, the drift is positive in both regions of increasing and decreasing RH at about $RH = 90\%$. The drift is dependent on the time of exposure of the particle to the specific RH. In order to check that, a second much faster (10 times faster) cycle was performed and is described in the humidogram in Fig. 5.2, right graph. This cycle is now almost completely closed, and can be used for quantitative analysis. The voltage signal depends of course on the charge of the particle, and a loss of charge seems to be the (only) possible explanation if the cycles are not closed. The organics have a much lower dissociation constant than the inorganic salts like AS [54]. The number of net charges distributed on the particle is therefore much higher in relation to the absolute number of ions in the particle. However, a complete study and evaluation of the work function necessary to extract ions or electrons from the particle is beyond the scope of this dissertation. A study with different charge to mass ratio and charge sign should be

**Figure 5.1:** Very slow hygroscopicity cycle of an AS+AA aerosol particle in the EDB (radius $r \approx 4\,\mu m$, constant temperature $T = 290\,K$, 1 month total time). RH evolution (right scale, black curve) and voltage (left scale). Different colors refer to different time intervals of the mass measurements. A positive drift in the mass even in regions of constant RH is evident.
5.1. Preliminary data analysis

Figure 5.2: Humidogram of the AS+AA experiments shown in Fig. 5.1 (upper graph). Lower graph: the same experiment together with a much faster one (black curve, roughly 1/10 of total time). This second hygroscopicity cycle is closed.

Carried out to understand this issue better. In the future, only closed or almost closed cycles will be used for the analysis, because in those cycles a possible charge loss does not complicate the analysis.

In cases like the one just described, the analysis of the radius of the particle and its comparison with the mass could be extremely helpful. The AS+AA mixture is not a good candidate for this scope, since the AA in the particle is always solid, and the radius can be optically calculated precisely only if the particle is completely liquid, as explained in Chapter 2.
Thus, a second slow hygroscopicity cycle was performed on AS+CA mixture, roughly 10 days long; see Fig. 5.3 for the time evolution of the experiment and Fig. 5.4 for the corresponding humidogram. Being CA always liquid in the particle, the optical radius can now be calculated (uppermost panel). The lowermost panel of Fig. 5.3 shows the mass of the particle and the RH in the chamber, while the middle panel shows the root mean square (RMS) deviation of the scattered light intensity, which indicates a small change in morphology due to the AS deliquescence (RH around 80%) and efflorescence (RH around 27%). Also in this case as well as in the previous one, a positive drift in mass is observed at $RH = 85\%$ both in the hydration and dehydration branches, and the consequence is that the cycle is not closed. Both cases in Fig. 5.1 and Fig. 5.4 show hygroscopicity cycles which are much longer than an usual one (typically from half a day to a complete day).

The radius measurements can be used to check if the size of the particle has changed. Figure 5.5 shows the time evolution of the radius (left scale) in regions of pretty constant RH (right scale). Colors are coded according to Fig. 5.4. The radius is constant within the precision of the radius measurements explained in Chapter 2. The “jump” between two radii of Fig. 5.3 and 5.5 are not due to experimental errors but are intrinsic of the analysis of Mie phase functions described in Chapter 2. Choosing the lower solutions, there is no detectable change (the constant dashed line is plotted to guide the eye), while choosing the upper solutions, the percentage of this change is only about 4%, which can not be responsible for the mass change observed (around 26% from 200 ks to 750 ks). A 4% change in radius would be responsible for a 13% change in mass. The radius calculations can be thus helpful especially where the mass ceases to be reliable. Moreover, the uptake of impurities or water can now be excluded as a cause for the previously observed anomalous drift in mass data. To conclude, only relatively fast hygroscopicity cycles which are closed can be quantitatively evaluated in these inorganic/organic mixtures.
Figure 5.3: Raw data of a very slow hygroscopicity cycle of an AS+CA aerosol particle in the EDB (radius $r \approx 5\mu m$, constant temperature $T = 290K$). Lowermost panel: mass (lower curve) and RH (upper curve). Positive mass drift in the region of constant RH is evident. Middle panel: RMS signal detecting a clear but small morphology change (if compared with pure AS of Fig. 2.5) indicating the deliquescence and efflorescence of AS. CA is instead always liquid. Uppermost panel: optical radius from Mie analysis.
Chapter 5. Hygroscopic properties, EDB measurements

Figure 5.4: Humidogram of the experiment shown in Fig. 5.3. The positive mass drift at $RH = 85\%$ is evident. A voltage failure happened around RH=50\% and a small efflorescence at $RH = 25\%$. The cycle is not closed with a 33\% discrepancy at $RH = 10\%$.

Figure 5.5: Time evolution of the radius and RH during the experiment of Fig. 5.3 with the same color-code. Initial time is now $t = 0$ for all of the three intervals. RH (lower curves) is constant and the radius as well (upper scattering), or at worst very slowly increasing (see text for details).
5.2 From radius to mass

It is often desirable to compare radius and mass measurements like in the present case of a parallel project where the mass changes are measured with the EDB and aerodynamic radii with the H-TDMA. The radius and mass of a homogeneous spherical particle relate, and can be calculated once its density is known simply through:

\[ m = \rho V = \frac{4}{3} \pi r^3. \]  (5.1)

The density is dependent on RH, and can be approximated by [55]:

\[ \rho = \sum_i (wt_i) \rho_i. \]  (5.2)

where \( \rho_i \) and \( wt_i \) are the density of pure water or pure solutes and the corresponding mass fraction in solution [56], i.e. \( wt = wt\%/100 \), being \( wt\% \) the concentration expressed in weight percent. With the EDB one measures the voltage which is proportional to the mass (see Chapter 2), this means that the voltage (V) and the \( wt \) are related through:

\[ \frac{wt_2}{wt_1} = \frac{m_{s2}/m_{t2}}{m_{s1}/m_{t1}} = \frac{m_{t1}}{m_{t2}} \propto \frac{V_1}{V_2}. \]  (5.3)

where the indexes 1 and 2 refer to two different RH, hence to two different concentrations of the aqueous aerosol particle, \( m_t \) is the total mass, \( m_s \) is the mass of solute. However, to quantify the water uptake, an assumption regarding the \( wt \) is necessary at a reference RH. Thus, the voltage can be normalized to match a bulk measurement of the same system when available, or assuming that the mass at \( RH = 0\% \) equals the mass of solute, i.e. there is no water left in the particle at the limit of dry conditions. The former approach is of course in a better agreement with the bulk measurements but can under/overestimate the water content at \( RH = 0\% \); see for instance [57] and [58] and Fig. 5.6, drawn with data from [57] and [59].

In this dissertation the latter approach is chosen, and thus terms like “dry mass” and normalized mass or mass growth factor (labelled as \( m/m_0 \)) refer to the mass at \( RH = 0\% \) and to the voltage measurements normalized with the voltage at very dry conditions (extrapolated to \( RH = 0\% \)).

At this point the density depending on RH can be calculated from Eq. 5.2 and the mass from the radius through Eq. 5.1:

Figure 5.7 shows the normalized densities (the factor \( \rho/\rho_0 \) in Eq. 5.1) of the previous equation for pure CA with three different methods: the one just described using EDB
mass measurements and the one using radius measurements from the Differential Mobility Analyzer at Paul Scherrer Institute (see Chapter 4). The third one is the linear approximation which one could use if only the density of the pure substance is known and the density at $RH = 100\%$ is the one of pure water, $\rho = 1 \text{ g/cm}^3$. From this figure one realizes that the density of the particle has to be calculated from the measurements and the choice of the linear fit introduces big errors especially in the region of interest between 20% and 80% RH. There is a discrepancy between EDB and H-TDMA in the order of 5-10% which actually affects the absolute mass assessment, but does not influence this analysis, where relative mass changes are studied, because the mass calculated from the radius has to be then renormalized to the "dry" mass.

![Humidogram of one CA particle](image)

**Figure 5.6**: Humidogram of one CA particle. Mass measurements made with EDB (black points) are normalized to match the bulk data (red circles). The particle seems to retain water (10% of the mass) even at $RH = 5\%$. Data source: [57] and [59].
Figure 5.7: Density as a function of RH for one CA aqueous solution aerosol particle calculated using mass (black curve) and radius (red curve) measurements. Comparison with literature data is shown. The method is explained in the text. The black thin line is the linear fit assuming that only the density of pure CA ($\rho = 1.665$ g/cm$^3$, i.e. the density of the dry particle, at $RH = 0\%$) and the density of pure water ($\rho = 1$ g/cm$^3$, i.e. the density of the particle at $RH = 100\%$) are known.
5.3 Pure Citric acid (CA)

Several hygroscopicity cycles of pure CA individual particles were performed. When the mass measurements are normalized to the dry mass as explained in the previous section (to obtain the so-called mass hygroscopic growth or mass growth factor), they present a reduced hygroscopic growth at high RH; see Fig. 5.8. The mass growth factor is 15% lower than the bulk values, which are expected to be very precise. The reason for the reduced hygroscopic growth derived from the voltage measurements is not clear yet. The reproducibility of these measurements is though very high. It is clear that for $RH > 90\%$ a small underestimate of the RH, in the order of 1-2%, leads to a big error in the mass, given the steepness of the curve in that region. But this is not enough to explain the situation depicted in Fig. 5.8. A correction to the voltage measurements, in order to minimize the reduced water uptake shown in Fig. 5.8, was included considering that the particle in the EDB experiences a drag force. However, the correction needed for the measurements to match the bulk values is huge (almost a factor of ten) compared to the one actually measured under dry conditions, whereas application of the Stokes Law to an RH of 80% would lead only to a factor of two, and it is not clear why the drag force for CA particles should be much higher than for other particles.

For the purpose of this section, we drop the task of giving a careful and complete description of the water uptake in terms of voltage. Only the range of values of the hygroscopic growth at $RH = 80\%$ (growth factor between 1.35 and 1.42) will be considered for analysis.

For this system, radius measurements are available for the whole range of RH, since the CA is always in liquid state in the particle. The method described in Section 5.2 to convert radius to mass is used, and the results are shown in Fig. 5.9. The amount and the scattering of the radius data (red circles) have been reduced calculating the median of the distribution every 5% step in RH (green spots). Data from literature are also plotted: black spots for EDB measurements and blue circles for bulk data. The mass is normalized to the bulk data at about $RH = 78\%$, for each dataset. The agreement with the literature is now very good, and becomes excellent when we skip the datapoints at $RH = 35\%$ and 40% where the error of Mie phase function analysis becomes larger due to the fewer fringes which are observed in the finite scattering angle range.

The same procedure can be repeated for all cycles; Fig. 5.10 shows the result of this analysis, together with bulk and EDB data from the literature. The mass has been normalized assuming $m = m_0$ in the extrapolation to $RH = 0\%$. The agreement is
Figure 5.8: Humidogram of one CA aerosol particle. Several hygroscopicity cycles are compared with bulk and EDB data from the literature. Mass was normalized to dry mass ($RH = 0\%$ extrapolation). EDB data from literature are normalized to the bulk data at $RH = 80\%$.

Figure 5.9: Radius and mass for a pure CA aerosol particle. The median (green spots) of the radius data (red circles) is calculated at each 5\% step in RH. The agreement with literature data from EDB (black spots) and bulk data (blue circles) is good.
Figure 5.10: Comparison between mass growth factors calculated from radius measurements as explained in Section 5.2 and literature EDB and bulk data. The median of the distributions (coloured lines) are calculated as in Fig 5.9.

now also quantitative, even though a small underestimate of the water uptake persists. The results of the mass growth factors calculated from voltage measurements and from the optical radius are summarized in Table 5.1.

Table 5.1: Summary of mass growth factors for citric acid at $RH = 81\%$ measured in the EDB. Growth factors are calculated from voltage signal ($g_f (V)$), see Fig. 5.8, and from the optical radius converted to mass ($g_f (r)$) as explained in the text, see Fig. 5.10 (literature value [57]: $g_f = 1.66$).

<table>
<thead>
<tr>
<th>Particle</th>
<th>Cycle</th>
<th>g.f.$(V)$</th>
<th>g.f.$(r)$</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1.42</td>
<td>1.58</td>
</tr>
<tr>
<td>2</td>
<td>1.40</td>
<td>1.55</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.38</td>
<td>1.48</td>
<td></td>
</tr>
<tr>
<td>4</td>
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<td>1</td>
<td>1.35</td>
<td>1.56</td>
</tr>
<tr>
<td>All</td>
<td>1.35-1.42</td>
<td>1.48-1.62</td>
<td></td>
</tr>
</tbody>
</table>
5.4 Ammonium Sulfate (AS) and Citric Acid (CA)

Mixture of ammonium sulfate with citric acid have been studied for three different mixing ratios of the solution, 1:1, 2:1 and 4:1 molar ratio AS:CA. The humidograms in Fig. 5.11, 5.13 and 5.15 show the results of the mass measurements. All of them have been compared with model calculation using the Zdanovskii-Stokes-Robinson (ZSR) approach. A description of this method can be found in Chapter 4. Shortly, it is simply assumed that each substance present in the mixture does not influence the hygroscopicity of the others. Thus, the total water uptake will be the sum of the single ones weighted with the mass fraction as expressed in the following relation:

\[ g_f(RH) = \sum_i (g_f(RH))_i w_i, \]

where \( g_f(RH)_i \) is the mass growth factor of each compound depending on relative humidity, and \( w_i \) the solute mass fraction. This approach is suited to predict the water uptake in hygroscopicity cycles after deliquescence of all components in the solution. To correctly calculate the hydration branch, the mutual influence of solubilities between solutes has to be taken into account. In this simple form, the ZSR approach is not able to do this.

Therefore, in this study the ZSR approach is only used to describe the water uptake of liquid particles. For AS+CA mixtures this means RH > 80% (deliquescence relative humidity of AS). In the 2:1 case, also the comparison with literature data is possible. All of the three mixtures are in good agreement with the model, except for the 1:1 case at high RH values.

The raw datasets of the hygroscopicity cycles are also reported in Fig. 5.12, 5.14 and 5.16. The morphology of the particle and its phase changes can then be monitored. The 1:1 mixture shows no efflorescence and deliquescence at all, the particle stays always liquid, even if its morphology presents some anomalies at dry conditions (middle panel of Fig. 5.12). The oscillations seen are due to the optical resonances described in Chapter 3.

In Fig. 5.14 the particle at low RH values is partly solid (AS fraction) and partly liquid (CA and water) up to \( RH \approx 80\% \) \( (t = 20000s) \) and the deliquescence of AS occurs. After that, AS never effloresces again till the end of the experiment. This is a confirmation that water soluble organic compounds alter the behavior of inorganic particles [60]. In this case, CA suppresses the efflorescence of AS. This was supported also by the fact that the particle only effloresced after injection but not during subsequent hygroscopicity cycles.
Figure 5.15 and 5.16 show the 4:1 mixture. The similarities with pure AS of Chapter 2 are evident: DRH and ERH well defined, growth factor close to the pure AS case. A small water uptake prior deliquescence of AS is observed: part of the solid core dissolves due to the presence of citric acid.

**Figure 5.11:** Humidogram of an AS+CA aqueous solution aerosol particle in the EDB, 1:1 mixture. See text for details.

**Table 5.2:** Summary of mass growth factors for ammonium sulfate / citric acid particles with different molar ratio, $RH \approx 80\%$. Bulk measurements are from this study. ZSR model is used (see Eq. 5.4).

<table>
<thead>
<tr>
<th>Mixture</th>
<th>EDB</th>
<th>Model</th>
<th>Bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>1.65</td>
<td>1.69</td>
<td>1.75</td>
</tr>
<tr>
<td>2:1</td>
<td>1.87</td>
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<td>1.87</td>
</tr>
<tr>
<td>4:1</td>
<td>2.03</td>
<td>2.03</td>
<td>2.03</td>
</tr>
</tbody>
</table>
5.4. Ammonium Sulfate (AS) and Citric Acid (CA)

Figure 5.12: Temporal evolution of one hygroscopicity cycle of an AS+CA particle in the EDB \((T=290K)\), 1:1 mixture. Lowermost panel: voltage proportional to the mass (black curve), and RH (red curve). Middle panel: light intensity fluctuation. Uppermost panel: optical radius. See text for details.
Figure 5.13: Humidogram of an AS+CA aqueous solution aerosol particle in the EDB, 2:1 mixture. See text for details.
5.4. Ammonium Sulfate (AS) and Citric Acid (CA)

Figure 5.14: Temporal evolution of one hygroscopicity cycle of an AS+CA particle in the EDB ($T = 290K$), 2:1 mixture. Lowermost panel: voltage proportional to the mass (black), and RH (red curve). Middle panel: light intensity fluctuation. Uppermost panel: optical radius. See text for details.
Figure 5.15: Humidogram of an AS+CA aqueous solution aerosol particle in the EDB, 4:1 mixture. See text for details.
Figure 5.16: Temporal evolution of one hygroscopicity cycle of an AS+CA particle in the EDB ($T = 290K$), 4:1 mixture. Lowermost panel: voltage proportional to the mass (black), and RH (red curve). Middle panel: light intensity fluctuation. Here one clearly sees the difference in morphology at the beginning of the cycle before deliquescence compared to the end of the cycle after efflorescence. Uppermost panel: optical radius. See text for details.
5.5 Ammonium Sulfate (AS) and Adipic Acid (AA)

Adipic acid has been identified in many atmospheric samples [61] [62]. Its study opens interesting questions concerning the way it affects the hygroscopicity of inorganic salts and the results of field measurements. For instance, in Chapter 4 ([63]) a parallel study of AS+AA hygroscopicity has been made using the tandem differential mobility analyzer, concluding that it is important to allow for sufficient residence time at the specified humidity to reach equilibrium before the hygroscopicity measurements. Here the hygroscopicity of AA and AA+AS is quantified using the electrodynamic balance.

One may think, given the fact that AA is moderately soluble in water and has a very low hygroscopicity, that measurements of single particles containing AS and AA are straightforward: AS takes up water while AA does not, and thus the total uptake is simply the one calculated through Eq. 5.4. In fact, this is not exactly the case; discrepancy from "model" behavior have been observed with both EDB and DMA. Moreover, mass transfer limitation between gas and condensed phase occurred, see Chapter 4.

The low solubility of AA in water, leads to almost negligible water uptake and to the large scatter of the optical radius calculation because of the permanently solid nonspherical particle in the EDB after injection.

Figure 5.17 shows the temporal evolution of a single AA aerosol particle hygroscopicity cycle in the EDB. The mass (lowermost panel, black curve) is only slightly varying over the entire cycle (less than 5%) described by RH red curve, indicating no significant water uptake. This is also seen in the radius data, since the mean or median radius does not change during the experiment. The morphology of the particle exhibits no important changes (middle panel), and the radius (uppermost panel) can not give any supplementary size information for the reason explained above. The spread of the radius data points and the absence of distinct glare spots (not shown here) present in the near field CCD camera signal (see Chapter 2) indicate a solid non-spherical particle.

Mixture of AA with AS were studied with varying mass ratio of the two components. Radius measurements are no longer present in this section; they are all similar to the one in Fig. 5.17 and represent only an indirect evidence of AS+AA particles either completely solid or with a solid inclusion (the AA fraction).
Figure 5.17: Temporal evolution of one hygroscopic cycle of an AA particle in the EDB ($T = 290$ K). Lowermost panel: voltage proportional to the mass (black), and RH (red curve). Middle panel: light intensity fluctuation. Uppermost panel: optical radius.
5.5.1 Ammonium Sulfate and Adipic Acid, 2:1 mass ratio

Figures 5.18 and 5.19 describe two consecutive hygroscopicity cycles of an AS+AA particle, 2:1 mass ratio, in the EDB. The cycles (black and blue curves) are compared with the ZSR curve (in red). The ZSR model describes well the behavior of this aerosol particle: no significant water uptake before the deliquescence, DRH and ERH pretty much the same as in the pure AS case (see Fig. 2.4). The light intensity fluctuation data in upper panel of Fig. 5.19 show the increasing sphericity of the particle due to water uptake at $t = 15$ ks for the first cycle and $t = 45$ ks for the second one. The highest degree of sphericity though, is not reached abruptly, but slowly during the water uptake up to $t = 18$ ks and $t = 50$ ks. This is due to the presence of the solid AA fraction, the effect of which becomes weaker as long as water is taken up by the particle. The efflorescence points are evident in clear vertical shifts of the light intensity fluctuation datapoints at $t = 30$ ks and $t = 60$ ks. All the features of this experiment refer strongly to the presence of AS, whereas AA seems to be present as an inert mass.

**Figure 5.18:** Humidogram of an AS+AA aerosol particle, 2:1 mass ratio. Two consecutive hygroscopicity cycles (black and blue curves) are compared with the ZSR curve (red thin line). DRH and ERH are well defined and close to the pure AS case. Expected mass growth factor: $gf = 1.91$ at $RH = 81\%$. 
5.5. Ammonium Sulfate (AS) and Adipic Acid (AA)

Figure 5.19: Temporal evolution of two hygroscopicity cycles of an AS+AA particle in the EDB ($T = 290K$), 2:1 mixture. Upper panel: light intensity fluctuations. Lower panel: voltage proportional to the mass (black curve), and RH (red curve). See text for details.
5.5.2 Ammonium Sulfate and Adipic Acid, 1:1 mass ratio.

Figures 5.20 and 5.21 describe two consecutive hygroscopicity cycles of an AS+AA particle, 1:1 mass ratio, in the EDB. The cycles (black and blue curves) are compared with the ZSR curve (in red). The ZSR model describes well the behavior of this particle: no significant water uptake before the deliquescence, DRH and ERH pretty much the same as in the pure AS case. The mass increase at deliquescence ($RH \approx 80\%$) is now lower than for AS+AA 2:1 case due to the smaller amount of AS present for the same amount of AA. The light intensity fluctuation data in upper panel of Fig. 5.21 show the increasing sphericity of the particle during the water uptake at $t = 14\,ks$ and $t = 45\,ks$. In this case the difference before and after deliquescence is slightly less accentuated than in Fig. 5.19. In addition, the two efflorescence points are now not as evident from the light intensity fluctuation (the second one, in particular, detected only by a spike, but not by a shift of the data), but clearly appear in the mass loss (lower panel, black curve) at $t = 30\,ks$ and $t = 60\,ks$. All the features of this experiment refer evidently to the presence of AS and solid AA becomes visible in the light intensity fluctuation.

![Graph](image)

**Figure 5.20:** Humidogram of an AS+AA particle, 1:1 mass ratio. Two consecutive hygroscopicity cycles (black and blue curves) are compared with the ZSR curve (in red). Expected mass growth factor: $g_f = 1.68$ at $RH = 81\%$. 

AS+AA 1:1 w/w

- $EDB$ cycle 1 (this study)
- $EDB$ cycle 2 (this study)
- model
5.5. Ammonium Sulfate (AS) and Adipic Acid (AA)

Figure 5.21: Temporal evolution of two hygroscopicity cycles of an AS+AA particle in the EDB ($T = 290K$), 1:1 mixture. Upper panel: light intensity fluctuations. Lower panel: voltage proportional to the mass (black curve), and RH (red curve). See text for details.
5.5.3 Ammonium Sulfate and Adipic Acid, 1:3 mass ratio.

The electrodynamic balance technique works properly for particle size between 2 and 20 μm. The size of the particle after injection depends, apart from the characteristics of the injection system (see Chapter 2), on the total concentration of the solution prepared for injection. The 1:3 mass ratio solution at ambient temperature produce particles with a mass to charge ratio smaller than the ones obtained previously because of the low solubility of AA in water. This means non-trivial experiments with very low voltage to compensate the gravitational force of the particle, sometimes at the edge of the setup capability of keeping the particle in the EDB for an entire cycle. Some particles were lost either permanently or temporarily during the cycles. Nevertheless, many cycles were successful and led to the results described in the following.

Figures 5.22, 5.23 and 5.24 describe two hygroscopicity cycles of an AS+AA particle, 1:3 mass ratio, in the EDB. The cycles (black and blue curves, Fig. 5.22) are compared with the ZSR curve (in red). The particle starts uptaking water at RH ≈ 50%, well prior deliquescence. DRH is well defined and matching perfectly the model curve at RH = 81%. However, the two curves deviate from the model in the whole supersaturated region, retaining more water than in the model case. The efflorescence point at RH = 35% is very close to the pure AS (RH = 38–42%). After efflorescence occurs, there is a continuous loss of water for RH ≤ ERH.

The light fluctuations data of Fig. 5.23 (upper panel) confirm the water uptake prior deliquescence with a decrease of the signal at t = 20 ks, indicating that the particle is getting more spherical. Also detected are the deliquescence of AS at t = 30 ks and the dehydration in the supersaturated conditions up to t = 65 ks. The efflorescence of AS detected by the mass change at t = 70 ks only leads to a partial crystallization since the loss continues up to t = 80 ks, suggesting that the particle does not lose all of its water in one single step, but constantly after efflorescence. Similar behavior is exhibited by the second cycle plotted in Fig. 5.22 (blue curve) and described by the light intensity fluctuation in Fig. 5.24.

The discrepancy between experiments and model before the deliquescence and in the dehydration curve are most likely due to the morphology of the particle since several hygroscopicity cycles of the same particle show variation of the water uptake before DRH and of water release in the dehydration branch of the curve. As a further example, in Fig. 5.25 and Fig. 5.26 a hygroscopicity cycle performed with another particle with the same mixing ratio (AS:AA=1:3) is described. The pre-deliquescence water uptake is also present for this particle as for the first one at the same RH (mass increase at
5.5. Ammonium Sulfate (AS) and Adipic Acid (AA)

Figure 5.22: Humidogram of an AS+AA particle, 1:3 mass ratio. Two hygroscopicity cycles (black and blue curves) are compared with the ZSR curve (in red). Expected mass growth factor: \( g_f = 1.34 \) at \( RH = 81\% \).

\( RH \approx 50\% \) and fluctuation decrease at \( t \approx 20 \text{ ks} \). The deliquescence of AS and the growth factor at \( DRH = 81\% \) perfectly match the ZSR curve. The dehydration curve again deviates from the model and an abrupt loss of mass occurs at \( RH = 60\% \) (\( t = 65 \text{ ks} \) in Fig. 5.26), which is not reflected in a morphology change since this event is not detected by the light fluctuation signal (upper panel of Fig. 5.26). This can happen only if the released water was contained inside the particle pores. After this, the water is slowly released between \( 50\% \) and \( 40\% \) RH with a clear solidification of the particle during the time interval between \( t = 72 \text{ ks} \) and \( t = 75 \text{ ks} \) (mass decrease

Table 5.3: Summary of mass growth factors for ammonium sulfate / adipic acid particles with different molar ratio. ZSR model is used assuming that AA is an inert solid (see Eq. 5.4).

<table>
<thead>
<tr>
<th>Mixture</th>
<th>EDB</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>1.89 RH = 79%</td>
<td>1.91 RH = 80.5%</td>
</tr>
<tr>
<td>1:1</td>
<td>1.68 RH = 79.8%</td>
<td>1.68 RH = 80.5%</td>
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<tr>
<td>1:3</td>
<td>1.34 RH = 80.5%</td>
<td>1.34 RH = 80.5%</td>
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</table>
Figure 5.23: Temporal evolution of one hygroscopicity cycle of an AS+AA particle in the EDB ($T = 290K$), 1:3 mixture. Upper panel: light intensity fluctuations. Lower panel: voltage proportional to the mass (black curve), and RH (red curve). See text for details. Together with light fluctuations increase.)
Figure 5.24: Temporal evolution of one hygroscopicity cycle of an AS+AA particle in the EDB ($T = 290K$), 1:3 mixture. Upper panel: light intensity fluctuations. Lower panel: voltage proportional to the mass (black curve), and RH (red curve). See text for details.
Figure 5.25: Humidogram of an AS+AA particle, 1:3 mass ratio. Hygroscopicity cycle compared to the ZSR model curve. DRH and ERH well defined by mass changes but not by morphology changes. ERH is above the one of AS.
5.5. Ammonium Sulfate (AS) and Adipic Acid (AA)

Figure 5.26: Temporal evolution of one hygroscopicity cycle of an AS+AA particle in the EDB ($T = 290 K$), 1:3 mixture. Upper panel: light intensity fluctuations. Lower panel: voltage proportional to the mass (black curve), and RH (red curve). See text for details.
5.5.4 Pre-deliquescence water uptake

Special attention was paid in order to check if the pre-deliquescence water uptake observed for the ammonium sulfate/adipic acid particles (AS:AA=1:3 mass ratio) like the ones described in Fig. 5.22 and Fig. 5.25 are reversible processes with respect to relative humidity changes. Figure 5.27 shows the temporal evolution of two consecutive incomplete cycles, where the RH, starting from less than 10% is increased to 67% and then is lowered to reach very dry ambient conditions. The light intensity fluctuations (upper panel) are in opposite phase with the mass changes, indicating that the shape of the particle is getting more spherical while its mass and the RH are increasing. This is consistent with a water uptake which fills the pores of the solid particle because of the Kelvin effect, conferring it a more spherical shape and possibly a more homogeneous refractive index. By decreasing the relative humidity, the water evaporates, pores and cavities are depleted and the particle turns back to an irregular crystalline shape.

![Figure 5.27](image)

**Figure 5.27**: Temporal evolution of two hygroscopicity cycles of an AS+AA particle in the EDB ($T = 290K$), 1:3 mixture. Upper panel: light intensity fluctuations. Lower panel: voltage proportional to the mass (black curve), and RH (red curve). See text for details.

The details of this process are described in the companion study reported in Chapter 4. Here we focus on the pre-deliquescence water uptake detectable with the electro-
dynamic balance, which was not observed with the hygroscopicity tandem differential mobility analyzer used in Chapter 4. Several hygroscopicity cycles for different particles have been measured. Some of the cycles are incomplete because of experimental failures, or not closed, or not matching exactly the hygroscopic growth predicted by the ZSR approach. However, the region of the hygroscopicity cycles we are interested in, i.e. the pre-deliquescence for \( RH < 80\% \) is not involved in these problematics and has a high degree of reproducibility. The values used in the following analysis are summarized in Table 5.4.

It is known that the condensation of water in the micropores can be important for those materials which have a complex morphology [64], like the non soluble aerosol particles or the soluble ones with an inert solid component. The basic equation which controls the micropore condensation governs also drop formation in the atmosphere. The water vapor pressure which is in equilibrium with a curved liquid surface varies with the concavity or convexity: it is greater with increasing convexity and lower with increasing concavity. The relative humidity in equilibrium with the micropore radius \( r \) has been calculated by Thomson, later Lord Kelvin [65]:

\[
RH(r) = 100a_w \exp \left( \frac{2\sigma V_m}{rT \mathcal{R}} \right),
\]

where \( a_w \) is the water activity, necessary to apply the equation to saline solutions (see Chapter 4), \( \sigma \) is the surface tension of water (\( \sigma = 72.2 mJ/m^2 \) at \( T = 290 \) K), \( V_m \) is the molar volume of water and \( \mathcal{R} \) the gas constant.

The Kelvin equation will be applied in the following to illustrate the morphology effects on an AS+AA particle, 1:3 mass ratio. Let's focus on the hygroscopicity cycles of Fig. 5.22 zoomed in Fig. 5.28 for convenience. The particles start taking up the water at \( RH \approx 45\% \) and the water uptake reaches a maximum at \( RH \approx 55\% \) for the blue curve and decreases again to a constant lower value. This decrease might be due to veins and pores structures that coalesce and disappear because of the presence of water and the partial dissolution of AS. The black curve reaches a maximum pre-deliquescence water uptake at \( RH \approx 60\% \) with no subsequent water loss. The corresponding relative increases in mass around these values are roughly 7.5\% and 10\%. At a first degree of approximation, the internal cavities, pores and veins of the AS+AA particle can be described as one single cylindrical vein of radius \( r_v \) and length \( l_v \) (uppermost drawing in Fig. 5.29). For the black curve: the average \( RH \) between the onset and the maximum of the pre-deliquescence is \( RH \approx 53\% \) which is in equilibrium with a vein radius of \( r = 2.6 mm \) calculated through Eq. 5.5 assuming that \( a_w = 0.8 \) for a solution to form. The vein length follows after quantifying the mass of the water uptake simply from the
Table 5.4: Summary of measurements for ammonium sulfate / adipic acid particles, 1:3 mass ratio, in the electrodynamic balance. Reported values: relative humidity at the onset (Onset RH) and at the maximum (Pre RH) of the pre-deliquescence water uptake with the corresponding growth factor (Pre \( m/m_0 \)), the deliquescence relative humidity (DRH) and the corresponding growth factor (DRH \( m/m_0 \)).

<table>
<thead>
<tr>
<th>Particle</th>
<th>Cycle</th>
<th>Onset RH%</th>
<th>Pre RH%</th>
<th>Pre ( m/m_0 )</th>
<th>DRH%</th>
<th>DRH ( m/m_0 )</th>
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<tr>
<td>Summary</td>
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</table>

formula for a cylindrical volume and from the density definition:

\[ l_v = m_v/\left(\rho_v \pi r_v^2\right), \]

(5.6)

where \( m_v \) is the mass of liquid in the vein and \( \rho_v \) its density, which is assumed to be the one of water for simplicity. The optical radius of the particle in the EDB can not be exactly calculated for this particular system because it is always non spherical; never-
Figure 5.28: Pre-deliquescence water uptake for the cycles in Fig. 5.22. Vertical lines from left to right indicate the onset RH and the maximum water uptake for the two hygroscopicity cycles (black and blue curves). ZSR model in red.

Nevertheless a rough estimate can be inferred by the spread datapoints like in the uppermost panel of Fig. 5.17. Additionally, the knowledge of the concentration of the solution used for injection (which is proportional to the particle size after injection) can support this estimate of a particle radius of $r \approx 3\mu m$. The particle density is known from Eq. 5.2 ($\rho = 1.462\ g/cm^3$), and thus the absolute mass of the particle and hence of the water uptake can be easily calculated considering the 10% relative water uptake estimated above. From Eq. 5.6, a vein length of $l_v = 77cm$ turns out; this huge number, compared with a $3\mu m$ particle size, has to be taken as an evidence of the highly complex morphology of the particle necessary to accommodate the taken up water.

The same analysis, can be repeated using of course different more realistic geometries in order to describe the surfacial and internal morphology of the particle. For instance, a rugged surface made of semi-spherical pores with the same Kelvin radius $r = 2.6nm$ can be envisaged (middle drawing in Fig. 5.29). This surfacial structure can be reproduced in a number of similar underlying layers necessary to accommodate the 10% water uptake shown in Fig. 5.28. Repeating the calculation above for this geometry leads to 105 layers with a width of 2.6 nm per layer. The high degree of complexity of
the particle morphology is again confirmed.

The highest degree of morphology complexity would be the one which describes the particle as a packing of spherical voids with a radius equal to the Kelvin radius calculated above (lowermost drawing in Fig. 5.29). The AS+AA material would be in the lattice of this arrangement, with discontinuities which allows water to penetrate the particle and fill the voids. The problem of packing a sphere or a cube with small spheres (which in the present situation would represent the pores) is an old one in mathematics, starting with Kepler in the 17th Century and still a matter of discussion with last papers published just a couple of years ago [66]. The percentage of filling ranges from 50% up to 77%, confirming that a high pre-deliquescence water uptake in pores structures is in principle possible but not realized to such an extent for the AS+AA particles which take up water between 5% and 15% at low relative humidity.
Figure 5.29: Particle morphology for an AS+AA particle, 1:3 mass ratio. The complex morphology of the particle is thought to be responsible for the pre-deliquescence water uptake observed in the measurements (see Fig. 5.28). Three different structures are used to explain this effect. The particle is internally crossed by a single vein of radius given by the Kelvin equation (uppermost drawing), it can have several rugged surface layers (middle drawing) or contain spherical voids (lowermost drawing). See text for the details of calculation.
Chapter 6

Conclusions and Outlook

6.1 White light spectroscopy

A novel and simple technique to measure very small relative size changes of a single micron-sized aerosol particle in an electrodynamic balance (EDB) was presented. This technique uses a ball-lens LED as "white" light source to excite optical resonances of the intensity of light scattered by the particle. A simplified treatment of the Mie theory of scattering for spherical particles allows the analysis of the spectra without the exact identification of the order of resonance. Instead, the shift of the spectra peaks due to the change in size of an evaporating particle are monitored and, the radius rate of change can be calculated consequently. A useful application of this technique is the measurement of the enthalpy of vaporization and vapor pressure of compounds in aqueous solution aerosol particles.

This approach was tested on aqueous malonic acid particles, an organic substance of atmospheric importance. The validity of this approach was confirmed; vapor pressure and enthalpy of vaporization were measured as a function of relative humidity, and hence of the concentration of the particle, for different ambient temperatures: \( \Delta H^o = 100 \pm 17 \text{ kJ/mol} \) for the enthalpy of vaporization, \( p_o = (3.2 \pm 1.2) \times 10^{-4} \text{ Pa} \) for the supercooled melt at a standard temperature of \( T^* = 298.15 \text{ K} \), and \( p_{sat} = (4.1 \pm 1.6) \times 10^{-5} \text{ Pa} \) for the vapor pressure of the saturated malonic acid solution particle.

The technique is particularly suitable to those substances with very low vapor pressure, or for measurements at elevated relative humidity, where common analysis made with a fixed wavelength source can be inadequate. It is estimated that the lowest vapor pressure measurable is about 2 orders of magnitude smaller compared to a fixed wavelength technique. For instance, it might be of use when determining binary activity
coefficients [33]. This novel approach has potential to become a relatively simple and cheap method for sizing spherical homogeneous in either optical or electrodynamic traps.

### 6.2 Hygroscopic properties, H-TDMA measurements

Some inorganic/organic mixed-phase aerosol particles (size 50-100 nm) were studied with a hygroscopicity tandem differential mobility analyzer (HTDMA). Of particular interest for this dissertation is the mixture ammonium sulfate / adipic acid (AS+AA) where the adipic acid is present in the solid phase regardless the relative humidity values. As a consequence, AA encapsulates some of the AS in veins and/or pores leading to mass transfer limitation of the system: the water uptake rate of the AS is slowed down by solid phase diffusion. Thus, it is important for hygroscopicity measurements of such mixtures to allow for a sufficient residence time in the H-TDMA in order to reach equilibrium.

### 6.3 Hygroscopic properties, EDB measurements

The hygroscopicity of micron-sized aerosol particles made of two organic acids of atmospheric importance, citric acid (CA) and adipic acid (AA) together with an inorganic salt, ammonium sulfate (AS), was investigated using an EDB. Numerous hygroscopicity cycles were performed in order to study the influences of those organics on the hygroscopic features of AS for different mixtures of the AS+CA and AS+AA systems.

The mixture AS+CA showed a depression of both deliquescence and efflorescence relative humidities with increasing the CA fraction. For the 1:1 molar ratio mixture the particle does not deliquesce or effloresce, and is thus always in liquid phase. The 2:1 system instead, shows efflorescence only after injection in the EDB; once the particle deliquesces the efflorescence does not occur again. In the 4:1 case the hysteresis due to the presence of AS is present but the water uptake starts before deliquescence of AS. All of these features affect the solid-to-liquid partitioning of aerosol particles in the atmosphere and water-soluble compounds play a role in the direct and indirect aerosol effect as well as in heterogeneous chemistry.

Particles made of AS+AA are always either solid or with a solid fraction, because AA never deliquesced during these experiments. The presence of a solid inclusion
6.4. Outlook

The new LED technique shown in Chapter 3 may be used to measure, under varying ambient conditions, the vapor pressures of several organics of interest for atmospheric science. It may also be helpful to investigate the artifacts of both H-TDMA and EDB for some substances which are proved to be difficult to characterize hygroscopically, like the case reported in literature of glutaric acid where EDB and H-TDMA give qualitatively different results.

The influence of organics on the hygroscopicity of inorganic compounds alters the behavior of inorganics in a non trivial way which needs to be better understood given the richness of organic chemistry and the presence of organics in every tropospheric aerosol sample.
Appendix A

Formaldehyde: Absorption on Sulfuric Acid droplets

Introduction. Formaldehyde is the simplest carbonyl compound in the atmosphere and, being a precursor to “odd hydrogen” (OH-+HO2) family, is important for cleaning the troposphere and lower stratosphere. The partitioning between gas and aerosol phase will thus strongly influence the atmospheric OH chemistry [67], [40].

We report measurements of the long time period uptake of gaseous formaldehyde into the condensed phase of aqueous sulfuric acid and ammonium sulfate particles.

Experimental Setup. The experiments are performed with single, micrometer sized particles levitated in an electrodynamic balance under tropospheric temperature and humidity conditions (see Chap.2 for a complete description of the experimental setup). The uptake of formaldehyde by the condensed phase is monitored in situ over a time period up to a week by independently analyzing the mass change of the particle, monitoring the radius change and change of physical state by means of elastic light scattering as well as analyzing the chemical composition by Raman spectroscopy.

Uptake of HCHO on H2SO4 particles. A second phase with different refractive index forms, changing the optical properties of the sulfuric acid droplet. This is observed in panels (a),(b),(c), of Fig.A.1 showing the microscopic image of the particle, by a distortion of the glare spots depending on the position of the new phase and the appearance of an additional spot. A distortion of the two-dimensional angular scattering pattern in the far field is also observed in panels (e),(f),(g). Panel (d) and (h) refer instead to an Ammonium Sulfate particle which experienced the same treatment of the previous one. No second phase forms in the particle, and no change in its optical properties is detected.
In addition, a very broad fluorescence signal is observed in the Raman spectra. Shown in Fig.A.2 are spectra of a sulfuric acid droplet (radius about 5 μm) with an initial H₂SO₄ concentration of 30 wt% (trace 1). With increasing concentrations of H₂SO₄, the intensity of the OH stretching vibration at about 3400-3600 cm⁻¹ becomes smaller (trace 2). At a concentration of 85 wt% (trace 3), a broad fluorescence signal is superimposed and is typically 2-3 orders of magnitude stronger than the Raman spectrum. The fluorescence still interferes with the Raman lines when the droplet is diluted back to 35 wt% (trace 4) and the water signal has decreased significantly.

**Kinetics of uptake.** We use the intensity fluctuation data to quantitatively measure the kinetics of HCHO uptake. [H₂SO₄] ≈ 70 wt%, p(HCHO)≈ 500 ppb, T = 255 K. The time evolution of the experiments is shown in Fig.A.3.

The volume of the second phase forming can be estimated from the intensity fluc-
Figure A.3: Kinetics of the uptake described by intensity fluctuation of the scattered light. Fig. A.4 shows a linear time dependence over the first day of uptake (filled symbols). A similar timescale is observed in bulk experiments (open symbols). A second phase forms at high acid concentrations which does not dissolve again after water uptake. Polymerization is the most likely process into play, e.g. [68].
Figure A.4: Volume determination of the new forming phase.
Appendix B

Hygroscopicity study: Glutaric Acid and Ammonium Sulfate

This Appendix is a summary of measurements of Ammonium Sulfate (AS) / Glutaric Acid (GA) single aerosol particles levitated in an electrodynamic balance (EDB).
Figure B.1: Pure GA. Upper figure: Temporal evolution of a typical experiment with the particle trap. Lowermost panel: relative humidity (red curve) and DC voltage proportional to the particle mass. Middle panel: The light intensity fluctuation data give information about the asphericity of the particle. Uppermost panel: optical radius from fringe patterns. Lower: humidogram of the experiment compared with literature data.
Figure B.2: Pure GA. Humidogram of consecutive hygroscopicity cycles with a zoom on the efflorescence region.
Figure B.3: Pure GA. Left: Temporal evolution of a typical experiment with the particle trap. Lowermost panel: relative humidity (red curve) and DC voltage proportional to the particle mass. Middle panel: The light intensity fluctuation data give information about the asphericity of the particle. Uppermost panel: optical radius from fringe patterns. Right: humidogram of the experiment compared with literature data.
Figure B.4: AS+GA 1:1 molar ratio. Humidogram of an hygroscopicity cycle compared with literature data.
Bibliography


[8] Notes from the first summer school on Aerosols, Heterogeneous Chemistry and Climate.


[40] Seinfeld, John H. / Pandis, Spyros N. Atmospheric Chemistry and Physics From Air Pollution to Climate Change, 2006, John Wiley & Sons


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