Hygroscopic Properties of Mixed Ammonium Sulfate and Carboxylic Acids Particles

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The hygroscopic growth of internally mixed ammonium sulfate and carboxylic acid particles was measured as a function of relative humidity by using a tandem differential mobility analyzer (TDMA). In TDMA experiments the organic compounds with different solubilities act in several ways, ranging from the behavior of totally insoluble substance to that of soluble compounds. The hygroscopic properties for mixtures containing either adipic acid or phthalic acid together with ammonium sulfate indicate that the organic fraction of the particles behaves as an inert mass and does not contribute to water uptake. The mixtures involving malonic acid or succinic acid increased the water uptake of the ammonium sulfate part only. The results indicate that the solubility of the organic fraction in individual aerosol particles clearly influences the aerosol–water interaction.

Introduction

The interaction between atmospheric aerosol particles and water vapor influences the aerosol properties and therefore also several phenomena in the atmosphere. One of the most investigated ones is the formation of cloud droplets in the troposphere. This process is initiated by preexisting aerosol particles, and the activation of an aerosol particle to a cloud droplet depends strongly on the chemical composition of the particle. Ubiquitous sulfate compounds [such as $(NH_4)_2SO_4$] are thought to be dominant chemical species in cloud condensation nuclei (CCN) (Pruppacher and Klett, 1997) and dissolve readily in water forming a highly concentrated aqueous solution at deliquescence, typically between 30 and 80% relative humidity (RH), depending on the actual chemical composition.

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The importance of the hygroscopic properties, particularly soluble volume (mass) fractions, of aerosol particles to cloud droplet formation has been shown in model studies (Kulmala et al., 1996). Formation and growth of cloud droplets vary as a function of particle size and soluble mass fraction. It was shown that the smaller, more hygroscopic particles can activate in many cases more easily than the larger, less hygroscopic ones.

Field experiments using a tandem differential mobility analyzer (TDMA) at RH of about 80–90% show that individual lower tropospheric particles include both hygroscopic compounds (such as inorganic salts) and an inactive fraction. The inactive fraction is usually assumed to consist of insoluble organic compounds (McMurry and Stoltzenburg, 1989; Svenningsson et al., 1992, 1994; Swietlicki et al., 1999; Zhang et al., 1993). However, little is known of the actual organic compounds and their interaction with water. Recently, several field and laboratory studies have been conducted in order to

get more information on the hygroscopic properties of the organic fraction of aerosol particles.

Saxena et al. (1995) analyzed observations of particle chemical composition and water content from a continental nonurban (Grand Canyon) and urban (Los Angeles) location to determine whether the water content of atmospheric particles is influenced by the presence of organics. They found that the hygroscopic properties of inorganic particles were altered substantially when organics were also present. These alterations can be positive or negative, depending on location and therefore probably the chemical composition of organics. Recently Dick et al. (2000) investigated the amount of water associated with organic carbon compounds during the Southeastern Aerosol and Visibility Study. They studied the water activity of the organic fraction of the aerosol over a wide range of relative humidities (5–85%) and concluded that organic-associated water content is considerably less than that of sulfate compounds for high RH, but comparable with or greater than for low RH.

It seems obvious that the water-soluble organic compounds have a potential to play a significant role in aerosol–water interactions in the atmosphere. However, compounds that are only slightly soluble in water (or aqueous salt solutions) may also play an important role in cloud droplet activation. The effect of slightly soluble compounds on cloud droplet activation has been studied by Shulman et al. (1996). They concluded that cloud droplet growth is affected by two mechanisms: (1) by gradual dissolution in growing droplets, which affects the shape of the Köhler curve; and (2) lowering of surface tension, which decreases the critical supersaturation.

Saxena and Hildemann (1996) thoroughly reviewed water-soluble organics in atmospheric particles. They concluded that the molecular composition of fine particulate organics is poorly characterized because the particles contain hundreds of organic compounds that cover a wide range of carbon numbers, functional groups, and solubility. If the organic compounds are water insoluble, they may form micelles or surface films that can prevent the condensation or evaporation of water from particles. On the other hand, water-soluble organic compounds will absorb water in order to remain in equilibrium with water vapor. These compounds can either exhibit deliquescence or be completely hygroscopic at all RH values.

A few studies have investigated the effect of organic coating on the hygroscopic growth and deliquescence of aerosol particles. Hansson et al. (1998) investigated the effect of organic coatings on the hygroscopic properties of laboratory-generated NaCl aerosol particles. They observed a slight lowering of the deliquescence relative humidity and suppression of growth for the coated particles. Interestingly, the growth suppression was surprisingly low, even when a significant mass of organics (equal to the mass of the salt crystal) was deposited on the salt particles. Similar results were obtained by Andrews and Larson (1993), who found that a film of organic surfactant lowered the deliquescence RH for NaCl particles. In addition, their results indicated a decrease in the hygroscopic behavior of the inorganic particles due to the surfactant coating.

The hygroscopic growth of internally mixed particles consisting of both inorganic salt and organic fraction was recently investigated by Cruz and Pandis (2000). They found no changes in the deliquescence of the inorganic salts [NaCl, $(NH_4)_2SO_4$] for the studied mixtures. They also concluded that the growth characteristics of the mixed particles can be reasonably well approximated with an assumption that both the inorganic salt and organic compound absorb water independently. In other words, if the detailed chemical composition of individual particles is known, an estimation of the growth factor can be calculated. However, more detailed investigations by Cruz and Pandis (2000) showed more complex interaction between the inorganic and organic fraction of the particles, which may be positive or negative concerning the water uptake of the particles.

In this study, we determine the hygroscopic growth characteristics of internally mixed particles containing ammonium sulfate and selected organic compounds in RH-controlled TDMA measurements. The selected compounds are typically found in atmospheric aerosol particles and are potentially important in aerosol–water interactions. The selected organic compounds vary in water solubility. The aims of the present study are (1) to provide information on the behavior of potential/typical atmospheric inorganic–organic mixtures in TDMA experiments (simulating the experimental procedure of field studies), and (2) to provide experimental data that are needed in further theoretical studies.

Experimental Studies

TDMA

The growth characteristics of internally mixed aerosol particles (that is, mixture within individual particles) were measured using a TDMA technique. In general, this system can be used in studies of the processes leading to size changes of particles. The results are usually presented as a growth factor (that is, increase in diameter) due to the humidification of dry particles. The size range of the instrument is limited practically to submicrometer particles due to inertial and gravitational losses in the system. In this study, the dry size of 100 nm was selected for a number of reasons. This size represents accumulation-mode particles in the ambient aerosol. This particle size has relatively a long life in the atmosphere (several days), and therefore can influence global phenomena. In addition, 100 nm is large enough that the Kelvin curvature effect can be neglected.

The TDMA system that is used in this study is described in detail by Hämeri et al. (2000) so only a short summary is given here. The TDMA instrument includes DMA1, the RH conditioner, DMA2, and particle counter. The DMA1 is used to classify particles of known size from the polydisperse input aerosol. The humidity of sheath air of DMA2 is controlled, and the size of the dry particles entering to DMA2 adjusts to the prevailing RH (mixture of aerosol air and sheath air). The resulting particle size is measured with DMA2 and the particles are detected with a condensation particle counter (CPC, TSI Inc. 3010).

Experimental procedure

The experimental setup is shown in Figure 1. A polydisperse aerosol was generated from an aqueous solution with an atomizer. The aqueous solution was prepared mixing care-

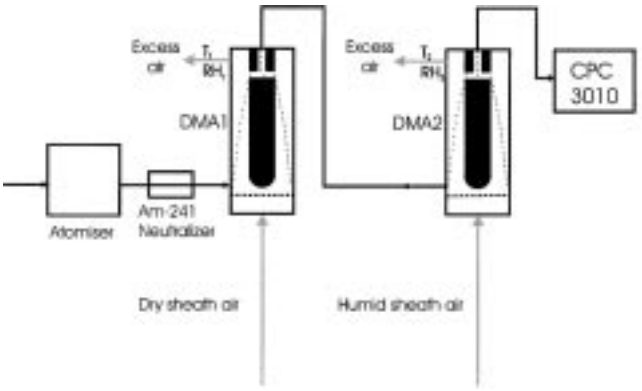

Figure 1. Experimental setup.

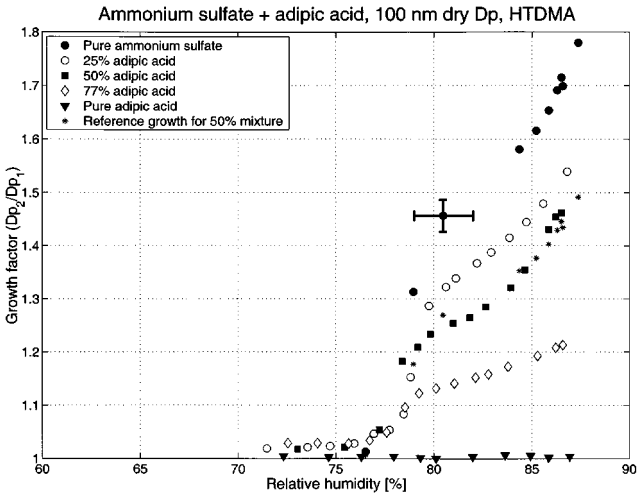

Figure 2. Growth factor for 100 nm dry particles consisting of different mixtures of ammonium sulfate and adipic acid.

The uncertainty of the experimental data is indicated as error bars for one data point. See text for explanation of the error analysis.

fully weighed amounts of ammonium sulfate and the selected organics with deionized milli-Q water. In order to ensure a complete solution with slightly soluble compounds, the solutions were heated to ca. 50°C overnight (10 h) in a closed bottle. The final solutions were all subsaturated at room temperature. A pure ammonium sulfate solution was made by mixing 2.64 g salt with one liter of water, resulting in an 0.02-mol/L solution. When other mixtures were prepared, the total mass of solutes was kept constant in order to obtain relatively stable output aerosol spectra from the atomizer. As an example, 50% of both substances by mass was a mixture of 1.32 g of both substances with one liter of water. Since the molar masses of all the substances used were relatively close together, the proportion by mass was close to that by mols.

Droplets from the sprayer were mixed with dry air to solidify the particles. The RH of the dry polydisperse aerosol was typically $<10\%$. However, there is no experimental information on the structure of the generated particles. One of the key questions is the potential presence of liquid water in dry particles. This would influence the response of the particles to increasing relative humidity and therefore the interpretation of the data. Nevertheless, at this stage we assume that the particles are dry and the observed growth takes place between a dry crystal structure and a solution droplet. The diluted dry aerosol passed through a charger (bipolar Am-241 neutralizer) and flowed directly to the DMA1, where a certain mobility of aerosol particles was selected. Assuming that there were no multiple charged particles and that the particles were spherical, the aerosol leaving the DMA1 should have consisted of a nearly monodisperse aerosol with a known mean size and size spread. The characteristics of this monodisperse aerosol are shown to depend on the aerosol and sheath air flow rates and on the classifying voltage (Knutson and Whitby, 1975).

The monodisperse dry aerosol entered DMA2, where RH conditioning took place. The sheath air of DMA2 was humidified to a certain value by mixing humid (RH approximately 100%) air and dry-air streams. The resulting relative humidity was measured using a dew-point sensor in the excess air flow. The accuracy of the dew-point sensor is on the order of $\pm 0.5\%$, or less, which is very good. However, there is considerable uncertainty of the true, representative RH value inside the DMA2. The main reasons for this uncertainty are: (1) the final RH inside the DMA2 results from mixing dry aerosol flow (0.5 Lpm) with humid sheath flow (10 Lpm). These two flows are laminar and the mixing of water vapor takes place due to diffusion. This process is relatively rapid as compared to the residence time inside the DMA2, but probably tends to sift the true value of RH lower than the measured one. (2) Second, the potential inaccuracy of the RH determination is related to the temperature of the DMA2. Even if the room temperature during the experiments were stable, there could have been temperature gradients inside the 50-cm-long DMA column. These gradients will result in

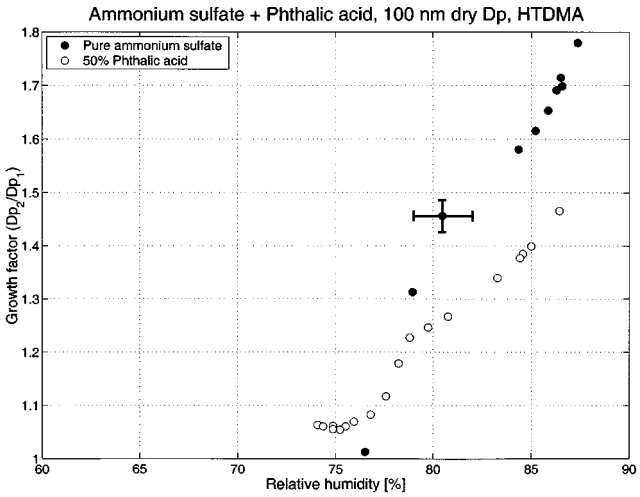

Figure 3. Growth factor for 100 nm dry particles consisting of ammonium sulfate and phthalic acid.

The uncertainty of the experimental data is indicated as error bars for one data point. See text for explanation of the error analysis.

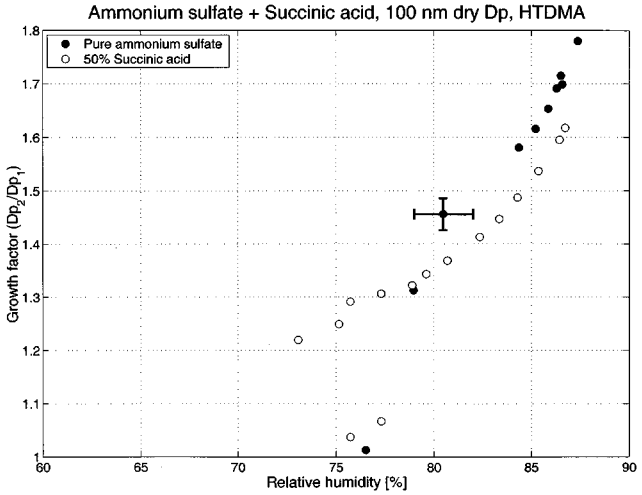

Figure 4. Growth factor for 100 nm dry particles consisting of ammonium sulfate and succinic acid.

The uncertainty of the experimental data is indicated as error bars for one data point. See text for explanation of the error analysis.

further error in the determination of the RH. For these reasons, the overall accuracy of the RH determination is concluded to be $\pm 1.5\%$, as indicated with the error bars in Figures 2–5. Further confirmation of this assumption was obtained with our recent measurements with $(NH_4)_2SO_4$ aerosol using a technically improved version of the instrument (Hämeri et al., 2000), which showed good agreement with previous measurements using the electrobalance method (Tang and Munkelwitz, 1993).

The size measurements were made by scanning the voltage of the DMA2. The accuracy of a DMA in determining the size is relatively good. In addition, this situation is even better, as the relative change in size was the primary interest. The major inaccuracy of the size determination comes from the inaccuracies in the flow determination. We estimated that the uncertainty of our measurements was ± 0.03 in the growth factor. This uncertainty is indicated as error bars in Figures 2–5.

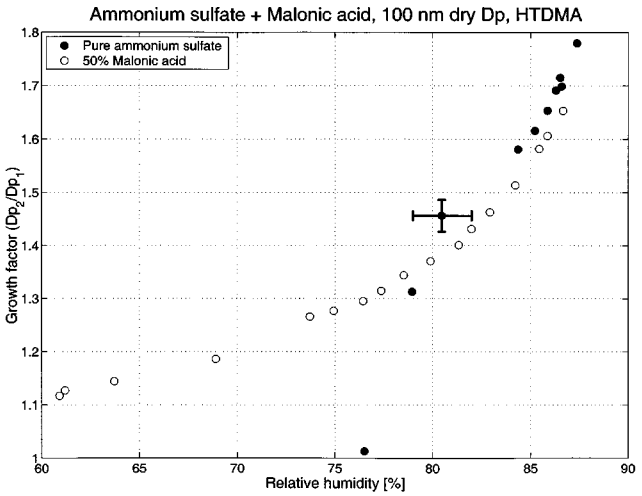

Figure 5. Growth factor for 100 nm dry particles consisting of ammonium sulfate and malonic acid.

The uncertainty of the experimental data is indicated as error bars for one data point. See text for explanation of the error analysis.

Aerosol flow through both DMA1 and DMA2 was 0.5 Lpm, and the sheath flows were 10 Lpm. Thus, the aerosol flow to sheath flow ratio was rather small (1/20), and the spread of the monodisperse aerosol was therefore relatively narrow ($\pm 5\%$ in mobility). The aerosol from the exit of the DMA2 was mixed with an additional 0.5 Lpm flow of dry filtered air, and the number of particles was determined using a CPC.

The TDMA setup used in this work was originally developed for hygroscopic growth measurements of ambient aerosol. The goal of the ambient measurements is typically to determine the growth factor at constant relative humidity (85–90% in our case). Therefore, the operation of the instrument was limited to a relatively narrow RH range (ca. 60–90%). However, the purpose of these measurements was to provide data that are useful for interpreting the ambient TDMA results.

Finally, we note that the measurements performed had relatively short residence times at various stages of the measurement system: 34 s between particle production (atomizer) and classifier (DMA1), 1 s in DMA1, 1.5 s between DMA1 and DMA2, and 4.4 s in DMA2 (where humidification and growth took place). The residence times in the atmospheric conditions that are of practical interest are typically much longer, and it is therefore possible that some slow dynamical processes did not have enough time to happen in the measurement system at 80–90% RH. The experiments presented in this article do not, however, indicate any mass-transfer effects.

The chemical compounds

In this study, the hygroscopic characteristics of particles internally mixed with ammonium sulfate salt, and organic compounds with different solubilities are investigated. The organic compounds selected all have significant concentrations in the atmosphere (Sempere and Kawamura, 1994; Saxena and Hildemann, 1996; Shulman et al., 1996). These compounds can be taken as model compounds, because of their range of water solubilities and surface activities.

The organic compounds investigated were adipic acid, phthalic acid, succinic acid, and malonic acid. These compounds belong to dicarboxylic acids and represent typical secondary organic compounds in the atmosphere. The proper-

Table 1. Properties of Investigated Compounds at 0°C

Component	Solubility in H_2O (mol/L)	Molecular Wt. (g/mol)
Adipic acid $C_6H_{10}O_4$	0.05*	146.14
Phthalic acid $C_8H_6O_4$	0.02*	166.13
Succinic acid $C_4H_6O_4$	0.25*	118.09
Malonic acid $C_3H_4O_4$	5.19*	104.06
Ammonium sulfate $(NH_4)_2SO_4$	12.6	132.14

*Shulman et al. (1996).

ties of the compounds are listed in Table 1. The solubilities in H_2O have been measured by Shulman et al. (1996). The solubilities range from low to moderate and high value. Unfortunately, the water activity data (gas-phase activity vs. mol fraction in the water solution) for these compounds were not available.

Results

The growth of particles as a function of relative humidity was determined, starting with dry particles and increasing the RH for each size scan. The raw data contain size distributions measured at a certain relative humidity. The mean size was calculated from the size distribution, and the growth factor [D_p(RH)/D_p(dry)] is obtained by comparing the resulting size with the original size at low RH (ca. 10%).

Adipic acid

In Figure 2, the growth factor for 100-nm dry particles, consisting of different mixtures of ammonium sulfate and adipic acid, is plotted against relative humidity. The growth of pure ammonium sulfate is plotted as a reference curve. It can be seen that the deliquescence takes place slightly below 80% RH [the value in the literature is 79.9% (Tang and Munkelwitz, 1993)], and after that value the particle size increases with increasing relative humidity. The humidity scans were done by increasing the mass fraction of the adipic acid. The mass fraction is shown as a percentage value in Figure 2. Increasing the amount of adipic acid clearly causes growth suppression, and finally, with pure adipic acid aerosol particles, no growth was detected.

The uncertainty of the experimental values is indicated for one data point. These error limits are related to the accuracy of the instrument and are discussed in the Experimental section. The error bars indicate two essential points: (1) the growth factor is estimated as within ± 0.03, which implies that the small values below about 78% RH are not significant; and (2) the actual RH determination is very uncertain. This indicates that within the experimental uncertainty, no significant difference is determined for pure ammonium sulfate compared to earlier data in the literature (Tang and Munkelwitz, 1993).

If the growth of mixed particles is assumed to occur only because of the presence of ammonium sulfate salt, and the growth factor for internally mixed aerosol particles is calculated accordingly, one finds that it agrees well with the observed growth factors. This observation is demonstrated in Figure 2, where the reference growth for a 50%/50% mixture of ammonium sulfate and adipic acid is calculated from the pure ammonium sulfate data, assuming that the organic fraction is completely insoluble. It seems that adipic acid, even with finite solubility, does not increase in the TDMA measurements presented, and therefore behaves similarly to insoluble compounds in TDMA measurements up to at least RH 88%.

Phthalic acid

The growth curve for the 50%/50% mixture of ammonium sulfate and phthalic acid is plotted in Figure 3. Phthalic acid is seen to behave similarly to adipic acid, which could be expected from their rather similar solubilities.

The deliquescence RH is close to that of pure ammonium sulfate. However, a slight smoothing of the deliquescence behavior was detected. This gradual deliquescence process, which finishes at ca. 79% RH, might result from an internal mass-transfer limitation of the particles during growth, since the growth time inside the DMA is only ca. 4 s. The growth factor at about 75% RH is difficult to explain. It is still close to unity, based on our estimated uncertainty limits. However, it has to be considered as potentially true growth, especially when compared to adipic acid mixtures.

To summarize, the behavior of adipic acid and phthalic acid in a TDMA were found to be similar to that of completely insoluble compounds, even though these compounds are soluble, for example, in fully developed cloud droplets.

Succinic acid

The growth curve for a 50%/50% mixture of ammonium sulfate and succinic acid is plotted in Figure 4. Succinic acid has water solubility that is approximately ten times higher than those of adipic and phthalic acids. Consequently, differences in the behavior were detected.

The growth factor of mixed particle is clearly higher than those of previous mixtures. While adipic acid and phthalic acid (50%/50% mixtures) had a growth factor of ca. 1.4 at RH 85%, the growth factor for the succinic acid mixture is more than 1.5. This indicates that organic compounds with properties similar to succinic acid can participate in forming solution droplets in the atmosphere, and therefore enhance the growth factor from that of inorganic electrolytes only.

The deliquesce behavior of mixed particles is seen to become less well defined. The particles seem to exist both as crystalline and solution droplets well below the deliquescence value of pure ammonium sulfate, which might result from some unknown phenomena during the particle generation. The data points at RH of about 76–78 show that during single experiments both dry particles and solution droplets are detected. This may be an indication of differences in the history of the particles; a fraction of the particles has been in contact with high RH, while other particles have not. However, such behavior was not observed with other measured compounds. Another possible explanation is the nonuniform population of the particles leading to two different types of particles. The other potential reasons are discussed in the following section. Unfortunately, there are no experimental data at lower RH values to indicate whether the mixture had any deliquescence behavior. At RH values higher than 79%, only solution droplets are found.

Malonic acid

The growth curve for a 50%/50% mixture of ammonium sulfate and malonic acid is plotted in Figure 5. As could be expected, this curve clearly differs from the other ones in this study. Malonic acid has much higher solubility in water compared with the other compounds, and consequently the growth factor of a mixed particle is close to that of a pure ammonium sulfate particle. At RH = 85% a growth factor of

approximately 1.55 was observed, compared with a value of 1.6 for pure ammonium sulfate.

The behavior of mixed malonic acid particles also differs in deliquescence properties from the other compounds presented in this study. While the other compounds seem to have little or no effect on the deliquescence compared with pure ammonium sulfate particles, malonic acid mixed particles showed no deliquescence, but instead showed a continuous change in size as a function of RH. Surprisingly, the deliquescence value of pure ammonium sulfate particles was not visible in the growth curve, indicating that the deliquescence properties of the mixture are completely different from those of pure ammonium sulfate aerosol.

Relating the results to atmospheric measurements obtained for malonic acid mixture particles, one can conclude that organic compounds with similar properties not only increase the growth rate from that due to inorganic salts only, but also that the deliquescence behavior is altered, even if a significant part of the growth is finally due to inorganic salt with well-defined individual deliquescence characteristics.

Discussion

Deliquescence and hygroscopic measurements were performed for internally mixed ammonium sulfate and carboxylic acid aerosols. We have shown that the mixed aerosol particles show hygroscopic behavior in TDMA measurements, depending largely on the aerosol mixture in question. At the one extreme, the mixed particles seem to behave as if the organic compound is totally insoluble and works only by adding the total mass of both dry particles and solution droplets. At the other extreme, the mixed particles show hygroscopic properties that are same or similar to those of common pure inorganic salts. In addition, the mixed particles can produce the deliquescence properties that are very similar to those of pure ammonium sulfate, but may also completely differ from the pure ammonium sulfate salt properties.

The results just shown are discussed in terms of the initial chemical compounds, that is, ammonium sulfate and the organic acid in question. However, when dissolved in water these compounds will be ionized, and during the generation of the atomized particles, most likely a variety of compounds are formed. This will affect the experimental results and make the interpretation of the results complicated. In addition, the crystallization of particles after the atomizer is not necessarily true for mixtures. Pure ammonium sulfate will crystallize at about 37% RH (Tang and Munkelwitz, 1994), which might not be true for the investigated mixtures. However, the significance of the results in this case is rather the application to ambient TDMA experiments. The potential effects are discussed separately in the following.

The organic compounds in our study that were least soluble—adipic acid and phthalic acid—behaved closely as an inert mass in individual particles (Figures 2 and 3). This seems natural considering the low solubility when compared with that of ammonium sulfate. Also, the experimental data for pure adipic acid (Figure 2) show that the hygroscopic growth factor is unity up to about 87% RH. The observed value for the deliquescence for these mixtures does not differ from the values of pure ammonium sulfate in the literature. The somewhat smooth behavior close to deliquescence is to a large part due to technical characteristics of the experimental setup, and we conclude that these experiments did not show any effect on the deliquescence. This conclusion is also supported by the recent study by Cruz and Pandis (2000), who draw a similar conclusion based on the large amount of data on mixtures of inorganic salt (NaCl or $(NH_4)_2SO_4$) and organic compound (glutaric acid or pinonic acid). Based on the fact that both adipic acid and phthalic acid are slightly water soluble, these compounds may, however, have clear effects on the Köhler curve and alter the growth process of cloud droplets (Shulman et al., 1996). These results show that one has to be careful when using measured ambient TDMA data as an input source for model calculations.

The situation is completely altered with the other two mixtures that were used. This is probably due to the clearly higher solubility of these compounds. Succinic acid's solubility is an order of magnitude higher than that of adipic acid or phthalic acid, and malonic acid's is two orders of magnitude higher (Table 1). Unfortunately, no experiments were made for pure organic compounds. The need for such experiments is obvious, and further experiments are suggested as future work in this field.

Particles produced by the mixture of ammonium sulfate and succinic acid showed hygroscopic growth that was increased from what is expected if the organic compound is an inert mass (Figure 4). This clearly demonstrates the ability of such organic compounds to enhance the water particle uptake. However, some features of the data need some discussion. The deliquescence of the mixed particles is changed from that of pure ammonium sulfate. While the effect is obvious, it is not possible to determine the true deliquescence value from the available data. At the lowest measured RH value, the hygroscopic growth already took place. When higher RH values were investigated, two different types of particles were observed. The other group of particles showed no significant hygroscopic growth while the other group showed systematically increasing values. There are two possible reasons for this observation: (1) the production of particles resulted (for unknown reasons) in chemically different particle groups, and (2) during the journey inside the TDMA instrument, the particles experienced different histories. One potential reason for these observations is related to the evaporation of the particles and is discussed below. However, future investigations are clearly needed. Nevertheless, the available data show that these particles have deliquescence properties that are different from those of pure ammonium sulfate.

Another subject that needs attention is the potential evaporation of the particles during the experiment. Care was taken to ensure that there was no evaporation from the solution that was used for particle generation. However, succinic acid has vapor pressure that is nearly two orders of magnitude higher than that of adipic acid (Saxena and Hildemann, 1996), and therefore evaporation of the organic part is possible between particle generation and detection. As a matter of fact, the vapor pressure of succinic acid is similar to that of glutaric acid, which was used in the study by Cruz and Pandis (2000). They observed partial evaporation on the order of 5% in diameter (original diameter 100 nm). Our experiments showed a decrease in the dry diameter of 5 ± 1 nm, which is in good agreement with the other study. However, the data presented in Figure 4 are compared with the measured size

of the dry particles (instead of the calculated size), and therefore this effect is taken into account. It is nevertheless possible that the evaporation of the dry particles differs from that of the solution droplets, and there is some additional uncertainty about the absolute values of the growth factor. This uncertainty is difficult to estimate, and it is not included in the error estimates shown in Figure 4.

The evaporation of a mixed particle is assumed to result as the organic fraction evaporates, while the inorganic part remains constant. Therefore, the final composition may have altered from that of the original mixture. The 5% (in diameter) evaporation of the mixed particles results to 14% evaporation of the total volume. Assuming that all the evaporated volume is organic, it will result in a final particle composition of 42%/58% (organic/inorganic). This, in turn, tends to increase the hygroscopic growth if the growth is greater due to the inorganic part. However, the potential increase in the growth factor due to this effect is not enough to explain the observed increase between 50%/50% mixtures of succinic acid compared to adipic acid of phthalic acid. This can be observed by comparing the 23%/77% data in Figure 2 with the mixed data in Figure 4. The partial evaporation, however, may provide an explanation of the two types of observed particles. Since the monodisperse input aerosol always has finite width, it is possible that particles of slightly different size may behave differently during evaporation, which in turn could separate particles in two growth groups at RH values below that of deliquescence of pure ammonium sulfate.

The observations made for particles generated from the ammonium sulfate and malonic acid mixture are similar to those made for the ammonium sulfate and succinic acid mixture. The solubility of malonic acid is about 20 times that of succinic acid and is comparable in magnitude to the solubility of ammonium sulfate. The alteration of the deliquescence behavior from that of pure ammonium sulfate aerosol is clear. As a matter of fact, no deliquescence value was found in the measured RH range, indicating that the deliquescence takes place either at an RH lower than about 60%, or that the aerosol does not exhibit any deliquescence behavior. We could not find a value for the equilibrium vapor pressure of malonic acid. Because malonic acid is the lightest of the examined dicarboxylic acids, it seems possible that it is among the most volatile compounds. However, the experiments with dry aerosol indicated that the evaporation was less than 2 nm (2%). A change in size of this magnitude is probably real, even if it's still within the uncertainty limits shown in Figure 5. Thus we conclude that the evaporation is possible in the case of aerosol produced from the ammonium sulfate and malonic acid mixture, but the significance is probably smaller than that of succinic acid. The 2% (in diameter) evaporation of the mixed particles results in 6% evaporation of the total volume. As with succinic acid, if we assume that all the evaporated volume is organic, it will result in a final particle composition of 47%/53% (organic/inorganic). This effect tends to increase the hygroscopic growth significantly less than it does for succinic acid, and is clearly not large enough to explain the water uptake of the particles.

The measurements presented in this article were made in almost the same way as many of the earlier field measurements with a TDMA system. One of the main purposes of this article was to provide reference data for interpretation of the field data. Despite the obvious limitations of the absolute deliquescence and hygroscopic growth values of the data presented, the article clearly provides new insight that is valuable in future field studies using the TDMA setup. In conclusion it can be said that, based on TDMA data, the organic fraction that has been concluded to exist in atmospheric aerosol particles can consist of slightly soluble compounds that do not grow in the experimental system. Or alternatively, the fraction in TDMA experiments that is thought to be inorganic salts may have been overestimated if the organic fraction made a significant contribution to the uptake of water in the particles. Put another way, measurements of the hygroscopic properties at 80–90% RH cannot be valid for describing the behavior of the particles in clouds at RHs larger than 99%, and one has to be careful when using measured TDMA data as an input source for model calculations. Since the atmospheric aerosol particles are mixtures of not only two but several compounds, information regarding the hygroscopic growth due to each chemical compound is very difficult to obtain.

Acknowledgments

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