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VAPOR SCAVENGING BY ATMOSPHERIC AEROSOL PARTICLES

BY

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ABSTRACT

Particle growth due to vapor scavenging was studied using both experimental and computational techniques. Vapor scavenging by particles is an important physical process in the atmosphere because it can result in changes to particle properties (e.g., size, shape, composition, and activity) and, thus, influence atmospheric phenomena in which particles play a role, such as cloud formation and long range transport.

In the modelling portion of this thesis, the influence of organic vapor on the evolution of a particle mass size distribution was investigated using a modified version of MAEROS (a multicomponent aerosol dynamics code) (Gelbard and Seinfeld, 1984). The modelling study attempted to identify the sources of organic aerosol observed by Novakov and Penner (1993) in a field study in Puerto Rico. Potential sources were hypothesized to be organic vapor emissions from either forest vegetation near the sampling site or from the ocean's surfactant layer followed by gas-to-particle conversion. Comparison of model parameters with literature values suggested that the observed organic aerosol was formed by nucleation and condensation of terpene vapor emissions onto a pre-existing typical marine aerosol size distribution. Organic vapor emissions from the ocean were found to be an unlikely source of the observed organic aerosol.

Experimentally, vapor scavenging and particle growth were investigated using two techniques. The influence of the presence of organic in a particle on the particle's hygroscopicity was investigated using an electrodynamic balance. It was found that, for a Tween80/NaCl system, having organic associated with an inorganic salt particle slowed the deliquescence rate of the particle. Additionally, for the Tween80/NaCl system the deliquescence humidity was lowered due to the presence of organic - suggesting an increase in particle hygroscopicity. It was also shown that the presence of an organic carbon (e.g., azelaic acid, Tween80 or dodecyl sulfate sodium salt) on a carbon black particle made the carbon black particle hydrophilic, while a pure carbon black particle was observed to be hydrophobic. The charge on a particle (which is required for study of a particle in the electrodynamic balance) was investigated theoretically and experimentally. Particle charge was found to have a negligible effect on particle growth in electrodynamic balance studies.

A prototype apparatus - the refractive index thermal diffusion chamber (RITDC) - was developed to study multiple particles in the same environment at the same time. Proof of concept experiments showed that it is possible to determine particle composition with time from changes in particle refractive index measured using the RITDC. Further refinements to the apparatus were suggested.

DEDICATION

To my sister Mary for always being there
(what a twinkie!)

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CHAPTER 1

INTRODUCTION

1.1 MOTIVATION

Aerosol particles are an ubiquitous component of the atmosphere and influence a wide variety of atmospheric processes. In recent years, a number of researchers have related atmospheric phenomena such as climate change and visibility degradation to the properties of atmospheric aerosol particles (e.g., Larson and Cass, 1989; Sloane, 1984; Rood et al., 1989; Novakov and Penner, 1993). The chemistry of precipitation and cloud water is also largely determined by the composition of atmospheric aerosol particles (Collett et al., 1991; Radke et al., 1980; Leong et al., 1982; Borys et al., 1988). Therefore, it is important to understand the chemical and physical processes which affect the atmospheric aerosol. It is particularly important to understand the mechanisms by which atmospheric particles scavenge other atmospheric constituents because scavenging alters the particle's basic characteristics - size, shape, composition, and phase (Seinfeld, 1986). These characteristics in turn determine the behavior of the particle in the atmosphere, including the particle's transport properties, residence time and light scattering properties. In this thesis fundamental research aimed at understanding vapor scavenging (limited to gas-particle interactions) with an emphasis on atmospheric systems is described.

Atmospheric particles scavenge vapor molecules (e.g., by condensation) and other particles (e.g., coagulation and riming). The focus of the research described here is vapor scavenging by aerosol particles of various compositions. An important example of vapor scavenging by particles in the atmosphere is the formation of cloud droplets. Aerosol particles which are capable of growing by addition of water vapor into cloud droplets are called cloud condensation nuclei (CCN). The ability of a particle to act as a CCN will depend on the composition of the particle and variables such as particle size, temperature, and the relative humidity. A particle composed of hygrophilic materials is more likely to scavenge water vapor than a hydrophobic particle, all else being equal. In the case of cloud formation by vapor scavenging, it is generally assumed that atmospheric sulfate is the major source of CCN (Hegg et al., 1990). More recently, however, Novakov and Penner (1993) have concluded that particles other than sulfate, specifically organic particles, might also act as CCN. Their observations at a marine site in Puerto Rico suggest that the contribution of organic particles to CCN concentrations was of the same order of magnitude as the sulfate particle contribution. This raises several questions regarding the generation and growth of organic CCN: 1) what are the sources of organic CCN; 2) how does the presence of organic in a particle influence its growth and growth rate?

In addition, in this research another factor is considered that may determine if a specific particle will

grow in the atmosphere by vapor scavenging, namely the presence of other particles, with possibly different compositions. Gas-to-particle conversion (which includes both vapor condensation and nucleation) is strongly influenced by particle number concentrations (Stern et al., 1987; Eisele and Tanner, 1993). Wagner (1995) has suggested that in an environment with limited water vapor present, the more hygroscopic particles will preferentially grow due to water condensation compared to less hygroscopic particles. The Wegener-Bergeron-Findeisen mechanism describes just such a competitive effect for clouds composed of ice crystals and supercooled water drops. The ice crystals grow by water vapor diffusion at the expense of the supercooled cloud drops and may eventually cause the droplets to evaporate to supply an additional source of vapor for crystal growth (Pruppacher and Klett, 1978). If organic and sulfate particles coexist in a cloud forming environment - will they exhibit behavior independent of their composition, or will there be competition for water vapor and the more hydrophilic particles - most likely the sulfate particles - be preferred sites for vapor condensation? In this thesis a prototype apparatus for investigating this question is described.

The chemical and physical processes occurring in the atmosphere are quite intertwined. Specifically, gas-to-particle conversion and competition for water vapor by particles will be influenced by the chemical composition of the particles involved. The chemical constituents (water, sulfates, and organics) mentioned in the above examples are among the most important components of the atmosphere. They are also representative of important classes of atmospheric compounds: soluble and insoluble, hydrophobic and hydrophilic, organic and inorganic, ionic and nonionic; and can exist in vapor, liquid, and solid phases. Thus, by considering a small subset of organic and sulfate compounds as is done in this thesis, much insight can be gained into atmospheric processes.

The research described here is aimed at answering questions about the interaction of vapors with particles and in relating a particle's history of gas-particle interactions to its fate in the atmosphere. The outline of the thesis is as follows: Chapter 2 describes modelling efforts investigating sources of organic in a marine aerosol. In Chapter 3 accomplishments with the EDB showing the influence of organic coatings on particle hygroscopicity are summarized. Chapter 4 is an analysis of the applicability of electrodynamic balance results to atmospheric systems. In Chapter 5 a prototype apparatus for investigating multiparticle growth in a controlled environment is described.

Using modelling, single and multiparticle experimental systems a 3-pronged approach is presented with the goal of improving our understanding of the growth of atmospheric aerosol particles focusing on the influence of organics on particle growth. The modelling portion demonstrates that particle number concentration influences the size range in which gas-to-particle conversion can change the composition of the aerosol. Valuable insight into the parameters which contribute to gas-to-particle conversion is

also obtained. The single particle studies with the electrodynamic balance isolate how the presence of organic in the aerosol might influence a particle's behavior in the atmosphere. With the electrodynamic balance it is demonstrated that an organic coating can influence particle hygroscopicity and change the rate of particle growth. The multi-particle experiments are a step back in order to look at the bigger picture by investigating the influence of a particle population on particle/vapor interactions. Having first investigated compositional effects in the single particle growth studies it is then shown how a population of particles of different compositions might grow.

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CHAPTER 2

POTENTIAL ORIGIN OF ORGANIC CCN OBSERVED AT A MARINE SITE

2.1 ABSTRACT

Observations by Novakov and Penner (1993) suggest that organic aerosol particles may make up a significant portion of cloud condensation nuclei (CCN), comparable, perhaps, to the sulfate aerosol contribution to CCN. Because organic CCN would influence the albedo and radiative properties of clouds and play a role in climate change, it is important to identify the sources of these aerosols. In their research Novakov and Penner assumed that particles larger than $0.05\ \mu\text{m}$ could act as CCN at supersaturation ratios of 0.5% water vapor. Therefore the origins of nucleation mode aerosol ($0.03 < dp < 0.1\ \mu\text{m}$) are the focus of this research.

In this research, a dynamic aerosol model (MAEROS, Gelbard and Seinfeld, 1984) is applied to explore potential sources of the nucleation mode organic aerosol observed at a marine site in Puerto Rico by Novakov and Penner (1993). Novakov and Penner measured the size segregated mass and composition of the atmospheric aerosol at this site and found that organic aerosol mass dominated the sulfate mass in the nucleation mode. The presence of organics in this size range suggests that these organic aerosol particles were generated by nucleation of a gas phase organic followed by condensational processes. Therefore identifying sources of the gas phase precursors is important to determining the origins of the organic CCN.

Back trajectory analysis (Merrill, 1994) shows that the air mass that Novakov and Penner studied was without continental contact for 12 days prior to being sampled. This implicates two possible sources for the gas phase organic: biogenic emissions from the Puerto Rican forest upwind of the mountain sampling site and emissions from the ocean surface. In this research both the forest and ocean source scenarios are explored. It is shown that the forest is more likely to be the ultimate source of the observed organic aerosol particles.

Using MAEROS (modified to include nucleation) and reasonable input parameters taken from the literature it is shown that an assumed organic vapor flux for the forest scenario, very similar to the measured biogenic fluxes reported by Zimmerman et al. (1988), generated size distributions similar to the observed aerosol. In contrast, the ocean seems unlikely to be the source of the organic particles as the actual organic vapor flux off the ocean is much smaller than the flux required by these simulations to produce a size distribution matching NP's observations.

2.2 INTRODUCTION

Novakov and Penner (NP) (1993) studied aerosol particle size and composition at a marine site (El Yunque) in Puerto Rico. They found that the organic aerosol mass dominated the sulfate aerosol mass in the smaller size range ($dp < 0.08 \mu\text{m}$). Additionally they showed that the number concentration of cloud condensation nuclei (CCN) calculated from measured sulfate and organic mass concentrations corresponded closely to CCN number concentrations directly measured (see Table 2.1a). (In calculating CCN concentrations from mass concentrations, NP assumed that any particle with dp greater than $0.05 \mu\text{m}$ would act as a CCN.) This correspondence and the predominance of organic mass in the smaller size range ($dp < 0.08 \mu\text{m}$) suggest that the observed CCN were derived largely from organic aerosols.

Because the organic carbon observed by NP constituted a major fraction of the measured submicrometer aerosol mass and because this species contributed with sulfate to the CCN population, it is of interest to identify the sources of these small-sized organic aerosols. In this modeling study possible organic sources of the NP aerosol were investigated by assuming an initial aerosol size distribution and a variety of aerosol sources, and then simulating the evolution of the aerosol over time. The simulated aerosol mass size distribution was compared to the inverted mass size distribution generated from a typical measured distribution. The model included nucleation and condensation of organic vapor onto existing aerosol particles and coagulation and deposition of aerosol particles.

Here a dynamic aerosol model (MAEROS, Gelbard and Seinfeld, 1980) is applied to the specific case of the Puerto Rico site studied by NP, to explore potential sources of nucleation mode organic aerosol. The influence of various parameters (e.g., vapor pressure and surface tension) on the evolving atmospheric aerosol size distribution is explored. As mentioned above, the observed organic mass distribution, when converted to number concentration, indicated a large number of small organic particles ($\sim 1639/\text{cm}^3$), most in the so-called nucleation mode ($dp < 0.1 \mu\text{m}$) with diameter of order $0.03 \mu\text{m}$. Particles in this size range derive from both the nucleation of atmospheric species and the condensation of hot vapors during combustion processes (Seinfeld, 1986). It is assumed that the observed nucleation-sized organic must derive from a gas phase organic which undergoes by gas-to-particle conversion (nucleation and condensation). Air mass back trajectories (Merrill, 1994) indicate that the sampled air must have spent at least 10 days over the ocean. Thus, there are two possible sources for the gas phase organic: emissions from the forest upwind of the mountain site on Puerto Rico and emissions from the ocean. Here, both the forest and ocean scenarios are explored, and it is shown that the former possibility is the more likely source of the observed organic aerosols.

2.2.1 Description of model

The original MAEROS code (Gelbard and Seinfeld, 1980) was a one dimensional model formulated to

calculate aerosol particle composition and mass concentration as a function of time and particle size. It includes the following aerosol processes: coagulation, deposition, condensation, and it allows time-varying source inputs of particles of different size and composition. MAEROS has several advantages over other aerosol models. For example, MAEROS predicts aerosol mass distributions, unlike many air parcel trajectory models which only predict total aerosol mass loadings with time. In this study the model simulations are compared with NP's measured mass distributions and so this feature is quite useful. MAEROS also includes condensation and coagulation processes which can be important for growing nucleation size aerosol particles to a size where they can act as CCN. For multi-component systems the code does not make assumptions about the composition of particles in each section, e.g., there could be pure particles of each component or some mixture of the components in each particle. Thus it is not necessary to define whether the aerosol is internally or externally mixed. (In any event, NP (1993) determined that the assumed mixing state did not significantly affect their calculations of number concentrations.) The MAEROS code is limited for this application in that it does not model chemistry or meteorology (e.g., rainout), considers only a single particle density, regardless of component composition, can simulate only one condensing/nucleating vapor, and assumes a well-mixed air parcel.

This modelling study's goal is to gain some insight into potential sources of organic CCN. It is assumed in this study that the nucleation of organic vapor is described by the equation for classical homogeneous nucleation:

$$J = \frac{p_{\text{org}}^2}{(2\pi mkT)^{1/2}} \frac{2v\sigma^{1/2}}{(kT)^{3/2}} \exp\left(-\frac{16\pi\sigma^3 v^3}{3(kT)^3 (\ln S)^2}\right) \quad 2.1$$

where J is the nucleation rate (1/sec),

- p_{org} is the vapor pressure of organic (g/m^3),
- m is the molecular mass of the organic (g/molec),
- k is Plank's constant (dyne-cm/K-molec),
- T is temperature (K),
- σ is organic surface tension (dyne/cm),
- v is organic molecular volume (cm^3/molec), and
- S is saturation ratio of organic ($p_{\text{org}}/p_{\text{sat, org}}$).

For homogeneous nucleation to occur two conditions must be met: 1) a supersaturation of the gas phase aerosol precursor must exist and 2) other sinks for this gas (e.g., condensation onto pre-existing aerosol) must be minimal. To test the possible sources of organic nucleation aerosol, a nucleation

routine based on classical nucleation (Equation 2.1) was incorporated into MAEROS. (A similar modification to MAEROS was made by Warren and Seinfeld (1985) as part of the development of a code called ESMAP - the Extended Sectional Multicomponent Aerosol Package.) The accuracy of this study's nucleation routine for water vapor nucleation was verified using the water parameters given in Seinfeld (1986). It was assumed that substitution of the appropriate organic parameters into the nucleation equation would yield reasonable organic nucleation rates.

The classical nucleation equation (Equation 2.1) was originally derived to evaluate the homogeneous nucleation rate of pure water (Seinfeld, 1986; Pruppacher and Klett, 1978). It should be noted, however, that the relationship between saturation ratio (S) and nucleation rate (J) (shown in Equation 2.1) is not well characterized and several other nucleation equations have been proposed. Depending on the nucleation equation used, the nucleation rates predicted can vary by many orders of magnitude (Springer, 1978). Nevertheless, for most compounds, classical nucleation theory gives the best explanation of experimental observations and can generally predict the saturation ratio for the onset of nucleation (Heist and He, 1994; Springer, 1978). Furthermore, recent laboratory studies on the aerosol forming potential of various organics have used homogeneous nucleation to interpret their results (e.g., Stern et al., 1987; Zhang et al., 1992). Hence, to investigate the nucleation rate of organics, parameters appropriate for Equation 2.1 were chosen. It should be noted that this modification of MAEROS allows for only one vapor phase species. Thus, the only gas-to-particle conversion processes considered are organic condensation and nucleation.

An additional caveat: while classical nucleation theory gives the best explanation of nucleation experiments performed under controlled laboratory conditions (Heist and He, 1994), atmospheric conditions may be much different. The typically low number concentration of particles in the marine atmosphere enhances the possibility of homogeneous nucleation due to the correspondingly low surface area for vapor condensation. However, in the atmosphere there will be many different gaseous components which may interact, e.g., water and sulfuric acid vapor. Temperature and pressure might fluctuate, e.g., due to updrafts, and vapor concentrations may be inhomogeneous. Nonetheless, classical nucleation theory provides a place to start.

MAEROS was designed to model particle deposition in a closed, windless, smooth-walled environment. To investigate the evolution of an aerosol size distribution in a natural environment it was necessary to modify MAEROS so that predicted particle deposition velocities are comparable to those observed for natural systems (e.g., Sievering, 1984). The modified deposition velocities are in the range calculated for sulfate particles when horizontal velocities are between 5 and 15 m/s, a range consistent with the measured velocities at the study site.

2.2.2 Approach

The primary purpose of this research was to identify potential sources of nucleation mode organic aerosol in a marine air mass. To do so, initial conditions (e.g., time scale and initial aerosol mass distributions) were defined and the sources and sinks of particles and organic vapor which would influence the evolution of the initial mass distribution were identified. Fluxes for organic and sulfate particles were assumed based on values reported in the literature and a constant flux of condensible organic vapor was injected into the air parcel. The organic vapor flux and accommodation coefficient were then adjusted until the predicted final sulfate and organic mass and number distributions at the "measurement point" (i.e., the end of the simulation) are close to those measured by NP. The organic vapor flux and accommodation coefficient were then compared with literature values and it was determined whether the simulated values were reasonable. If input values proved reasonable, the set of assumed sources and sinks were considered conceivable. Sample MAEROS input files for the forest and ocean scenarios are shown in Appendix A. Below the general modelling approach is described in more detail.

To begin, the NP observed size distribution data for the representative sample period April 9-11, 1992, was chosen for study. NP used an eight stage MOUDI impactor to obtain their sulfate and organic aerosol mass distributions. The eight section mass distributions were inverted using a Twomey inversion routine (Novakov and Penner, 1993) to get smooth curves for number and mass size distributions (Figure 2.1). For this research a 30 section mass distribution was generated using several super-imposed log normal mass distributions to match the NP inversion curve. Table 2.1a compares the mass and particle number characteristics for the measured sulfate and organic to the sulfate and organic represented by the 30 section MAEROS size distribution. These simulations were concerned only with particles with $dp < 1 \mu\text{m}$. As is shown in Table 2.1b removing particles with $dp > 1.0 \mu\text{m}$ lowers the system mass somewhat (compared to values in Table 2.1a) but has no measurable effect on particle number concentration. Particles greater than $1 \mu\text{m}$ are generated predominately by mechanical processes (e.g., suspension of plant debris and sea spray) rather than gas-to-particle conversion (Seinfeld, 1986) and thus are not particularly relevant to this study. In the interest of completeness, however, particle source rates were estimated which would maintain the observed super-micrometer particle mass concentrations for both the ocean and forest scenarios: these are given in Table 2.2. Figure 2.1 shows the portion of the 30 section mass distribution matching the inversion curve for $dp < 1.0 \mu\text{m}$ and the assumed initial size distribution.

The observed size distribution at El Yunque cannot be reproduced without assuming an initial aerosol distribution. The presence of an initial distribution is quite reasonable given the presence of a

background marine aerosol. However, the choice of initial size distribution will, in part, determine whether nucleation occurs (e.g., Stern et al., 1987). Because NP's observed sulfate and organic size distributions were quite similar to size distributions reported for remote marine regions (Figure 2.2a,b), the Twomey inversion of NP's measurements was used, with the modifications described below, for the initial size distributions. The nucleation mode peak of small organic particles ($dp < 0.07 \mu m$) was assumed not present in the initial size distribution (shown in Figure 2.1a). The assumed initial organic size distribution consisted of two mid-size peaks between $0.06 \mu m < dp < 0.9 \mu m$ but with less mass than given by the inversion of the observed data. Figure 2.2a compares the assumed initial organic size distribution (converted to a five section distribution for ease of comparison) with other organic five section size distributions measured at coastal sites. It is quite similar to the organic aerosol distribution measured at various remote marine sites by Cachier et al. (1986).

The sulfate size distribution observed by NP was used as the initial sulfate size distribution (Figure 2.2b) without modification. (Note, then, that sulfate sources and sinks must balance in the simulation to preserve the sulfate size distribution.) The median diameter and sulfate mass concentrations in this distribution are consistent with other measured marine sulfate distributions (Hoppel et al., 1986; Quinn et al., 1993). Table 2.1c further compares the masses and numbers of sulfate and organic particles measured by NP to typical values reported in the literature for remote marine particles. Both the mass and particle number observed by NP are quite similar to those reported in the literature. Simulations using a sulfur gas species as the condensing and nucleating vapor were not run in this study. Because NP's measured sulfate mass distribution is similar to typical reported marine measurements (Figure 2.2b) (Hoppel et al., 1986; Quinn et al., 1993) it was chosen as the initial sulfate mass distribution in this study. Sulfate particle sources were added to maintain the observed distribution against deposition so that the sources of sulfate mass balanced the sulfate mass sink.

For this case study there were seven variables in the MAEROS input file which could be adjusted to emulate different initial conditions. The importance of these individual parameters in determining predictions of the aerosol size distribution was investigated by varying one parameter and seeing the sensitivity of the modelled size distribution to the changes in the parameter. The results of this sensitivity analysis are presented after results from our Puerto Rico case study.

2.3 CASE STUDY - PUERTO RICO

Figure 2.3 depicts the air mass back trajectory (Merrill, 1994) for the April 9/10 sampling period. This trajectory is representative of trajectories for the entire sampling study. Prior to reaching the sampling site, the air parcel spent at least 12 days over the ocean without continental influence. Average residence time for submicrometer aerosols in the troposphere is between 5 and 7 days

(Eichmann et al., 1980; Cachier et al., 1985) thus aerosols must be produced in or injected into the air parcel during the 12 day trajectory. Wind velocities at the sampling site indicated that the parcel spent between 4 and 10 hours over the rain forest before being sampled 18 km inland at the mountain site. This suggests that the observed organic aerosol results from gas-to-particle conversion of organic vapor emitted by either the forest near the sampling site or the ocean over which the air parcel had passed. Figure 2.4 is a schematic of these two source scenarios and how they are treated in these simulations. Figure 2.4a depicts the forest scenario. For this scenario it is assumed that the air parcel originated over the ocean with an initial particle size distribution typical of remote marine air. The tropical forest between the ocean and the sampling site was solely responsible for inputs to the parcel. Figure 2.4b depicts the ocean scenario. In this scenario both the ocean and cloud processing are assumed to inject aerosol particles into the parcel while the ocean also supplied a flux of organic vapor. The effects of precipitation on aerosol removal are neglected; this is a reasonable assumption given that precipitation can be assumed to occur once every 10 days and that precipitation scavenging of nucleation aerosol is very inefficient (Pandis et al., 1994). For both scenarios it was assumed that the mixing height was a constant (1000 m for the forest scenario, 500 m for the ocean scenario) and that the air parcel was well-mixed, implying that the vertical profiles of the air parcel constituents (i.e., organic and sulfate) do not change with height.

2.4 RESULTS

2.4.1 Forest scenario

The forest surrounding El Yunque Peak in Puerto Rico is categorized as a tropical forest. Mixing heights during sampling averaged about 1000 m (Merrill, 1994). As indicated earlier, the air parcel spent between 4 and 10 hours over the forest. For the forest scenario we assumed the air parcel arrived at the island coast with a typical remote aerosol size distribution (Figure 2.2a,b), and we used the MAEROS model to predict the size distribution's evolution. Organic and sulfate particles and a vapor source mimicking forest organic vapor production were injected into the parcel. The assumed initial size distribution ($dp < 1.0 \mu\text{m}$) had a total number concentration $595 \text{ particles/cm}^3$ (430 cm^3 sulfate, 165 cm^3 organic) and total mass concentration of $1.53\text{e-}9 \text{ kg/m}^3$ ($0.96\text{e-}9 \text{ kg/m}^3$ sulfate, $0.57\text{e-}9 \text{ kg/m}^3$ organic). Table 2.1c compares the mass and number concentrations of our initial size distribution with those reported in the literature for remote marine environments. Our initial total number concentration is on the high end of the reported values while our initial mass concentrations are comparable to other observations.

In the four and ten hour forest simulations, it was assumed that the initial organic mass distribution changed due to gas-to-particle conversion of oxidation products of the forest's organic vapor emissions and due to forest emissions of submicrometer organic aerosol particles. The organic vapor both

condensed onto pre-existing particles and generated new aerosol particles through homogeneous nucleation. To support the build up of particles near $0.5\ \mu\text{m}$ over loss by deposition required modelled submicrometer organic particle flux of $1.5\text{e-}12\ \text{kg/m}^2\text{-s}$ (equivalent to $1.5\text{e-}15\ \text{kg/m}^3\text{-s}$ source rate). The assumption of a larger initial size distribution in this size range would have required smaller emissions but tended to suppress the formation of a nucleation mode and hence was not explored further. Particles in the submicrometer range could be injected as plant wax particles (Beauford et al., 1975, 1977). Emission fluxes for fine particles ($dp < 2.1\ \mu\text{m}$) for an highly urbanized area have been estimated to be between 3 and $10\text{e-}12\ \text{kg/m}^2\text{-s}$ (Hildemann et al., 1995). Hence our suggested flux represents a reasonable guess. A forest can also emit larger supermicrometer organic aerosols in the form of spores, pollens, and other biogenic debris. A particle emission rate of $3\text{e-}14\ \text{kg/m}^3\text{-s}$ equivalent to a flux of $3\text{e-}11\ \text{kg/m}^2\text{-s}$ was required to maintain the observed organic particles with $dp > 1.0\ \mu\text{m}$, against deposition loss of the initial size distribution over the forest (Table 2.2).

Delmas and Servant (1983) estimated the dry deposition flux for submicrometer sulfate particles over a tropical forest to be approximately $5\text{e-}12\ \text{kg/m}^2\text{-s}$. In our simulations, the observed sulfate particle mode near $0.3\ \mu\text{m}$ diameter required a submicrometer sulfate particle emissions of $7.0\text{e-}12\ \text{kg/m}^2\text{-s}$ (median particle diameter $0.3\ \mu\text{m}$) to maintain its concentration against deposition. Assuming that this flux equals the dry deposition flux, we see that its value is close to that measured by Delmas and Servant (1983) over a tropical forest.

Forests emit a variety of organic vapors, the most significant of which are terpenes and isoprenes. Oxidation of these biogenic organics (e.g., by reaction with ozone or hydroxyl radical) can lead to condensable products (e.g., pinonic acid) which can undergo gas-to-particle conversion (Pandis et al., 1992). Previous research has suggested, however, that isoprene is not an aerosol precursor under typical atmospheric conditions (Grosjean and Seinfeld, 1989). This results from the fact that even though measured emission fluxes of isoprene are approximately four times greater than terpene fluxes, the vapor pressures of the isoprene reaction products are too high for the products to readily undergo gas-to-particle conversion. It is thought, therefore, that gas-to-particle conversion of terpene reaction products is the main source of biogenic aerosols, attributable to the low saturation vapor pressures of the terpene reaction products (Pandis et al., 1991; Kamens et al., 1981). Thus we ran simulations using organic parameters appropriate for the condensable oxidation products of terpene. Terpene emissions from plants vary as a function of leaf temperature. For a temperature change of $\pm 5^\circ\text{C}$, the model of Guenther et al., (1993) predicts terpene emissions vary by a maximum of a factor of two. In this work terpene emission rates will be assumed constant.

Figure 2.5a shows the final organic size distribution resulting from a four hour simulation using the

input parameters as given in Table 2.3. This simulation assumed a constant vapor emission rate ($7.4\text{e-}11\text{ kg/m}^2\text{-s}$) of a surrogate terpene reaction product into the air mass. For this scenario both nucleation and condensation are observed. The reaction yield for condensible terpene products is equivalent to approximately 10-50% of the primary terpene emission rates (Table 9, Grosjean and Seinfeld, 1989). This reaction yield and the simulated emission rate of reaction product give an emission rate of terpene (approximately $1.5\text{e-}10\text{ kg/m}^2\text{-s}$) that is larger, but of the same order of magnitude as terpene emission rates reported in the literature (e.g., $5.8\text{e-}11\text{ kg/m}^2\text{-s}$ by Zimmerman et al. (1988); $6.5\text{e-}11\text{ kg/m}^2\text{-s}$ by Guenther et al. (1993)). Altschuller (1983) noted a factor of five difference in measured fluxes from vegetation, thus our estimated terpene flux is quite reasonable. Because terpene and condensible vapor concentrations are closely correlated (given the 50% yield) it is reasonable to compare the modelled reaction product concentration with measured terpene concentrations. The concentration of uncondensed and unnucleated vapor at the end of the simulation was $9\text{e-}10\text{ kg/m}^3$ corresponding to a mixing ratio of 0.16 ppbv. This compares nicely with the typical ambient terpene vapor concentrations of 0.1-1.0 ppbv cited by Zhang et al. (1992), and 0.6-1.7 ppbv cited by Altschuller (1983).

In these simulations (see Table 2.3) the modelled total particle mass ($dp < 1.0\text{ }\mu\text{m}$) is $1.71\text{e-}9\text{ kg/m}^3$, the same as the inverted observed data (Table 2.1b). As Tables 2.1a and 2.3 show, there is also good agreement between measured (CN) ($1900/\text{cm}^3$), calculated total number ($2289/\text{cm}^3$) and modelled total number ($2007/\text{cm}^3$) concentrations. However, the shape of the nucleation peak (Figure 2.5a) does not agree particularly well with the shape of the inverted data curve. This is acceptable, however, given the both the modelled and measured uncertainties. The simulated final size distribution has a narrow nucleation peak at $0.03\text{ }\mu\text{m}$, the assumed nucleation diameter, because coagulation, which could broaden the distribution, is not significant for the nucleation mode aerosol during the four hour simulation. The nucleation-sized aerosol was input into the size distribution in a narrow size range (a single size bin is specified in the code). A more realistic simulation would have assumed that the condensible organic vapor formed a range of sizes of nucleation mode aerosol. Because the shape of the mass distribution determines the number distribution, variations in mass distributions caused by the simulation's assumptions could easily cause variations in the number concentrations consistent with the discrepancies between observed and simulated number concentration seen here. The effect of nucleation size is discussed further in the sensitivity study later in the paper.

A 10 h forest scenario was also considered (see Table 2.3). This scenario used slightly different source rates and accommodation coefficients. As can be seen in Figure 2.5b the simulated organic mass distribution for the ten hour period also matches well with that observed by NP. Comparing Tables 2.1a and 2.3, the total mass ($1.71\text{e-}9\text{ kg/m}^3$) again agrees with the NP observed mass, while total

modelled number concentrations ($2005/\text{cm}^3$) fall between the measured CN concentration ($1900/\text{cm}^3$) and the ($2289/\text{cm}^3$) number concentrations obtained from inverting the observed mass distribution. Once again the number concentration difference can be attributed to the narrowness of the nucleation peak. Back-calculating from the simulated condensable organic source rate of $3.0\text{e-}11 \text{ kg/m}^2\text{-s}$ (Table 2.3) gives a primary terpene flux of $6.0\text{e-}11 \text{ kg/m}^2\text{-s}$ (again assuming 50% conversion to aerosol precursor). This terpene flux is also consistent with terpene fluxes reported in the literature.

2.4.2 Conclusions: forest scenario

For the forest scenario it was found that the simulation time scale is too short for particle deposition to dramatically change the particle size distribution. This means that the organic vapor flux is essentially the net flux required to generate the desired organic particles. Thus, in the forest scenario the emphasis is on the gas-to-particle conversion and determining the parameters which will give us the correct ratio of condensation to nucleation. Our results are consistent with the assumption that the nucleation size organic aerosol observed at El Yunque was the product of the forest emissions. The simulation used realistic values for the initial organic and sulfate particle size distribution at the coast, realistic saturation vapor pressures, and organic vapor fluxes, to reproduce an organic nucleation peak that was similar to that observed by NP at their sampling site. Comparing the four and ten hour simulations, we see that the four hour simulation required an organic vapor flux that was a factor of 2.5 larger than the organic flux used in the ten hour simulation. This is because the other initial conditions are the same for both simulations (i.e., initial size distribution, particle sources) and thus a higher organic vapor flux will be required to simulate the same amount of gas-to-particle conversion in a shorter time period.

The most questionable parameter in these simulations was the choice of nucleation particle diameter (see sensitivity analysis presented below). This diameter ($0.03 \mu\text{m}$) chosen was approximately an order of magnitude larger than the diameter calculated using the Kelvin equation to determine the critical cluster size ($0.001 \mu\text{m}$ at $J_0 = 1/\text{cm}^3\text{-s}$). However, this nucleation diameter is approximately the same order of magnitude as the effective nucleation diameters of $0.01 \mu\text{m}$ and $0.074 \mu\text{m}$ experimentally determined by Stern et al. (1987) and Zhang et al. (1992), respectively.

2.4.3 Ocean scenario

While forest emissions of terpenes are one explanation for the organic nucleation aerosol observed by NP, the ocean could provide another source of organic vapor to act as an aerosol precursor (e.g., Marty and Salot, 1982; Eichmann et al., 1980; Greenberg et al., 1992). Nucleation mode sulfate aerosols can also be generated over the ocean. For example, Hoppel et al. (1986) have suggested that DMS at the ocean surface is the source of sulfate aerosols in the nucleation and accumulation mode size ranges.

However, in this section we present results for simulations assuming the nucleation mode aerosols were generated solely by organic vapor emissions from the surfactant layer on the sea surface. The generation of sulfate CCN due to gas-to-particle conversion of sulfur-containing gases was not studied in this research. It was shown earlier (Figure 2.2b) that NP's measured sulfate mass distribution agreed well with reported marine sulfate distributions (Quinn et al., 1993; Hoppel et al., 1986). Thus, the focus is on organic gas-to-particle formation; the sulfate mass distribution is treated as though it were at steady state by balancing sources and sinks of sulfate aerosol in the simulations.

Air parcel back trajectories (e.g., Figure 2.3) show that the air parcel had moved from east to west along the trade winds over the Atlantic Ocean before being sampled. For the trajectory time (12 days) the air parcel did not interact directly with continental sources suggesting that the organic aerosol observed was not of primary anthropogenic origin unless it was emitted near the sampling site. The initial aerosol size distributions chosen for the ocean scenario were the same as for the forest scenario (Figure 2.1ab). In this scenario it was assumed that the air parcel spent 10 days over the ocean and that the parcel's brief time (4-10 h) over Puerto Rican forest prior to sampling had no influence on the measured size distributions. The marine boundary layer height was assumed to be 500 m.

It was necessary to inject particulate sulfate into the air parcel in order to maintain the observed sulfate distribution. Assumed sulfate particulate fluxes at $0.09\ \mu\text{m}$, $0.3\ \mu\text{m}$ and $1.0\ \mu\text{m}$ of $5\text{e-}14\ \text{kg/m}^2\text{-s}$, $5.9\text{e-}13\ \text{kg/m}^2\text{-s}$ and $1.5\text{e-}13\ \text{kg/m}^2\text{-s}$, respectively, maintained the sulfate particle mass in these size ranges. Particulate sulfate over the ocean is produced by several mechanisms: in-cloud oxidation of SO_2 during non-precipitating cloud cycles; condensation of H_2SO_4 ; and heterogeneous nucleation of H_2SO_4 and water vapor (Hoppel et al., 1986; Pandis et al., 1994; Charlson et al., 1987). An average DMS flux from the ocean has been estimated to be about $5\ \mu\text{mole/m}^2\text{-day}$ (Pandis et al., 1994). This would be equivalent to a flux of $7.6\text{e-}12\ \text{kg/m}^2\text{-s}$ of sulfate as ammonia sulfate. Assuming that sulfate in the particle phase is produced solely by gas-to-particle conversion of DMS oxidation products our particulate source rates suggest that about 10% of the oceans' DMS flux undergoes gas-to-particle conversion. This compares well with the 16% conversion of DMS to sulfate in the Gulf of Mexico cited by Luria et al., (1989).

Sub and super micrometer sea salt particles are produced by sea spray and bubble bursting. Laboratory studies have suggested that submicrometer sea salt particles will contain enriched amount of organics from the ocean surface layer (Hoffman and Duce, 1976). Thus it is reasonable that our simulation consider an organic particle flux. In these 240 h simulations, an organic particulate flux of $3.5\text{e-}13\ \text{kg/m}^2\text{-s}$ was also necessary to maintain the organic aerosol mass concentration in the $0.6\ \mu\text{m}$ size range. This is very similar to Duce's (1978) estimated flux of $1.2\text{e-}13\ \text{kg/m}^2\text{-s}$ for organic

submicrometer particles from the ocean.

The composition of the observed organic aerosol was unknown. However, several research groups have studied organic compounds at the ocean surface. Compounds found include n-alkanes, fatty acids (e.g., carboxylic acids), fatty acid esters, and fatty acid alcohols (Eichmann et al., 1980; Marty et al., 1979; Gagosian et al., 1981). Because the composition of the organic was unknown, the saturation vapor pressure was assumed to be the same as that used in the forest scenario, $5.5\text{e-}11\text{kg/m}^3$ (0.01 ppbv). (Other researchers have assumed similar vapor pressure values. For example, Pandis et al. (1992) cited ranges between 0.003 and 2.0 ppbv, but assumed a typical oxidation reaction product had a vapor pressure of 0.002 ppbv in their study of urban organic aerosol formation.) As in the forest scenario simulations, the nucleation diameter was assumed to be $0.03\text{ }\mu\text{m}$. To generate nucleation aerosol and to achieve the same organic mass loading observed by NP, the flux of condensible organic vapor reaction products was $3.2\text{e-}12\text{ kg/m}^2\text{-s}$ (Table 2.3). Our results, discussed below, suggest that for our parameterization, the ocean is not a likely source of organic aerosol.

Figure 2.6 shows the predicted organic mass distribution for the ocean scenario. The resulting total number concentration was $1980/\text{cm}^3$ (Table 2.3). As in the forest scenario, the simulated nucleation peak is narrower than the nucleation peak for the observed inverted data. Again this can be attributed to the simulation directly injecting monodisperse nucleation particles into the air parcel. There are, however, two significant problems with the hypothesis that the ocean supplies the condensible organic vapor. First, we see that the organic vapor condenses on the peak at $0.3\text{ }\mu\text{m}$ in the sulfate size distribution so that we are unable to simulate the shape of NP's observed organic size distribution. Furthermore, our simulated organic vapor flux ($3.2\text{e-}12\text{ kg/m}^2\text{-s}$) is an order of magnitude greater than the oceanic flux calculated by Bonsang et al. (1988) for propane ($3.0\text{e-}13\text{ kg/m}^2\text{-s}$) and approximately equal to the oceanic n-alkane flux ($2\text{e-}12\text{ kg/m}^2\text{-s}$) estimated by Eichmann et al. (1980). Note, however, that our simulated flux is for a single unidentified condensible organic reaction product. Propane, which is not an aerosol precursor (Grosjean and Seinfeld, 1989), exists at higher concentrations and will have higher fluxes in the atmosphere than organic oxidation reaction products that do act as aerosol precursors. Back calculating from the reaction product fluxes used in the simulation, we can determine the flux of primary organic necessary to generate the secondary aerosol precursor vapor. If it is assumed that over the ocean the yield of condensible organic is 5% of the primary organic vapor (as is the case for n-pentadecane (Grosjean and Seinfeld, 1989)), then the primary organic vapor flux would be an order of magnitude larger than the flux of reaction products (i.e., approximately $6.4\text{e-}11\text{ kg/m}^2\text{-s}$). Assuming the vapor is n-pentadecane, this implies that the ocean must emit 200 times more n-pentadecane aerosol precursor vapor than it emits propane in order for the ocean to act as a vapor source for the nucleation. Alternatively, the oceanic n-alkane flux would need

to be 20-30 times higher than that measured by Eichmann et al. (1980). This is not a realistic expectation.

2.4.4 Conclusions: ocean scenario

The ten day simulation time for the ocean scenario (a factor of 60 longer than the four hour simulations) is more complicated than the four hour forest scenario. For the ocean scenario, there is enough time for the particles in the initial size distribution to deposit out, necessitating particle injection into the air parcel in order to simulate NP's observed size distributions. The depositing particles take organic from gas-to-particle conversion with them. Thus, to get the simulated system's mass to distribute as measured, we need to consider not only where the organic vapor goes in the size distribution (which depends on the relationship between condensation and nucleation), but also particle sources and deposition. The simulated organic vapor flux is therefore the total vapor flux needed to simulate the size distributions, not merely a net flux.

The influence of non-precipitating clouds on aerosol processing was not specifically addressed in this study, although the simulated sulfate particle source at $dp = 0.3 \mu\text{m}$ could be attributed to in-cloud aerosol production. Researchers (e.g., Pandis et al., 1994) have noted that the presence of non-precipitating clouds results in fewer nucleation mode aerosol and increased accumulation mode aerosol due to cloud droplet scavenging of both the nucleating vapor and nucleation mode (interstitial) aerosol. Such findings suggest that the organic vapor flux simulated in this study could be an underestimate of the organic flux needed to produce the observed organic mass distribution (assuming that cloud and organic vapor and particle interactions are similar to the SO_2 and sulfate vapor and particle interactions with clouds).

These simulations suggest that the ocean is not a reasonable source of organic vapor to form nucleation-sized particles. Although a size distribution similar to that measured by NP can be simulated, the organic vapor flux required to reproduce the nucleation size particles in the size distribution is much larger than would be expected for aerosol precursor vapor. At lower organic vapor fluxes, we found that the organic vapor preferentially condenses on the observed sulfate peak at $0.3 \mu\text{m}$ and nucleation is inhibited. It should be noted that the ocean/atmosphere is a complex environment to model and realistic simulations of ocean/atmosphere/ particle interactions require a model with meteorology and chemistry (e.g., the work of Pandis et al., 1994).

2.5 SENSITIVITY STUDY

MAEROS allows for the variation of many parameters. Since we are comparing the model results (the simulated size distributions) to observations (the observed NP size distributions) our model input must

be consistent with observations. Furthermore, it is important to understand the role the various parameters play in inhibiting or enhancing nucleation and the uncertainties in the values of the parameters used. Thus, this sensitivity analysis investigates the significance of each parameter for the specific conditions of the four hour forest scenario. The parameters studied in these sensitivity simulations, with the base case values following in parenthesis, were:

- mixing layer height (1000 m)
- particle density (1500 kg/m^3)
- accommodation coefficient of organic vapor (0.01),
- diameter of organic nucleation particle ($0.03 \mu\text{m}$),
- organic saturation vapor pressure ($5.5\text{e-}11 \text{ kg/m}^3 = 0.01 \text{ ppbv}$),
- surface tension (25 dynes/cm), and
- nucleation rate factor (1).

In what follows, we describe the influence of different parameters on model output for the 4 hour forest scenario. Parameters ranges were constrained based on ranges of values found in the literature. The results of the sensitivity study are summarized in Table 2.4. Table 2.4 compares the changes in system mass and number as a result of the individual parameter variation (and the percent change in mass and number) with the base case results of the four hour study.

2.5.1 Mixing layer height

The air parcel volume was assumed to be a well mixed volume 1 m^3 with the vertical dimension set at the mixing layer height. The mixing layer height was assumed to be constant. Thus, a factor of two decrease in mixing height is equivalent to a factor of 2 increase in source rate [s.r. = flux into volume/mixing height]. The mixing height was assumed to be 1000 m over the forest (Zimmerman et al., 1988) and 500 m over the ocean. As is shown in Table 2.4, the mixing height has a strong influence on the mass and number concentration of the air parcel. Pandis et al. (1994) studied the formation of CCN from sulfate precursors and came to the same conclusion about mixing height; in their model, changing the mixing height by a factor of two had a significant effect on their model results. For example, they observed a 40% increase in CCN number when they decreased the mixing height by half. Here, a decrease of mixing height by a factor of two increased CN concentration by a factor of 20. Using Pandis et al.'s (1994) definition of CCN (particles with $dp > 0.1 \mu\text{m}$ at $S = 0.1\%$) it was found in these simulations that the CCN number concentration increased by 9.7% for a factor of two decrease in mixing height.

The reasonableness of the assumption that the mixing height was constant should also be examined. Various investigators of organic vapor fluxes from forests (Greenberg et al., 1992; Zimmerman et al.,

1988) have noted that the mixing height over land varies in a 24 hour period. At night, as the atmosphere cools, the mixing height is lower, while during the day the height of the mixing layer rises at the rate of 1 - 10 m/min as the sun heats the earth's surface. If an average mixing height is chosen for the simulation, changes in mixing height will cancel out because the relationship between required organic vapor flux and mixing height is linearly proportional. Mixing heights over the ocean are less variable than over land because surface heating/cooling is not nearly so efficient over water and, changes in mixing height are typically ignored in marine modelling studies (e.g., Pandis et al., 1994, Raes and Van Dingenen, 1992).

2.5.2 Particle density

MAEROS is capable of handling up to eight aerosol components and one vapor species. However it only allows input of an average particle density for the entire system. In the Puerto Rico case study we investigated an air parcel containing both sulfate particles assumed to be ammonium sulfate with a density of 1769 kg/m^3 and unidentified organic particles with an assumed density of 1200 kg/m^3 . Our assumed base case particle density was 1500 kg/m^3 , but variation of the assumed particle density between 1300 and 1700 kg/m^3 had very little influence on the simulated final system mass or number (see Table 2.4).

2.5.3 Accomodation coefficient

The accomodation coefficient is defined (Jayne et al., 1990) as the ratio of the number of molecules absorbed by a surface to the number of molecular collisions with surface. The accomodation coefficient (also known as sticking coefficient) determines how readily a gas molecule which collides with a particle will stick to the particle. By varying the organic accomodation coefficient in MAEROS, it is possible to alter the ratio of condensation to classical nucleation occurring in the system. The smaller the accomodation coefficient is, the lower the ratio of condensation to nucleation. The amount of nucleation determines the number concentration of particles in the system while the system mass is predominately related to condensation. Figure 2.7 shows the interplay between mass and number concentrations as a function of the accomodation coefficient for different vapor source rates. The solid horizontal line lies along the observed mass and number concentration (i.e., the desired result). From Figure 2.7 we see that the combination of a vapor source rate of $7.3\text{e-}14 \text{ kg/m}^3\text{-s}$ and an accomodation coefficient of approximately 0.008 comes the closest to yielding our desired result.

There have been several studies aimed at measuring the accomodation coefficient of gases on particles and droplets. Baldwin and Golden (1979) investigated the accomodation coefficient of several atmospheric species on sulfuric acid and soot surfaces. They measured accomodation coefficients ranging from $1\text{e-}3$ to $1\text{e-}6$ (the lower detection limit of their study). The accomodation coefficient for

organics (alkanes and alkenes) on sulfuric acid were below their detection limit. Also, they found that the accommodation coefficient for SO_2 on soot was less than $1\text{e-}6$. Other studies (Gardner et al., 1987; Van Doren et al., 1990; and Mozurkewich and Calvert, 1988) studied accommodation coefficients of various atmospheric gases on aqueous drops and found accommodation coefficients ranging from 0.04-0.2 depending on factors such composition, temperature and relative humidity. Since accommodation coefficients are not well characterized for specific systems, and because the system we are simulating is very simplified (e.g., lacking in chemistry) it is difficult to say what an appropriate accommodation coefficient would be. In our modeling study we varied the accommodation coefficient between 0.0001 and 0.05. These values are within the range reported in the literature.

2.5.4 Nucleation size

According to classical nucleation theory, the critical particle nucleation size depends solely on the composition and concentration of the nucleation vapor and can be determined using the Kelvin equation (Seinfeld, 1986). However, the theoretical nucleation size is difficult to verify in experimental systems. For example, Zhang et al. (1991) studied the formation of aerosol from terpenes in a smog chamber. They observed the average particle size at the onset of nucleation to be $0.074\text{ }\mu\text{m}$ (with the smallest measurable diameter being $0.01\text{ }\mu\text{m}$) although classical nucleation theory yields a nucleation diameter of $0.002\text{ }\mu\text{m}$. Stern et al. (1987) estimated a nucleation cluster to consist of 100 molecules of the nucleating vapor. For the organics they studied (toluene and m-xylene) this is equivalent to a nucleation particle diameter of $0.003\text{ }\mu\text{m}$. At the high concentrations used in their experiments, condensation would occur quickly resulting in an effective nucleation size. Here effective size would be the nucleation particle diameter after rapid condensation of vapor onto the particle following nucleation. For the modelling part of their work they assumed this 'effective' nucleation particle diameter to consist of 200 - 500 molecules of the nucleating vapor equivalent to a particle diameter of $0.004 - 0.006\text{ }\mu\text{m}$. In their experiments, however, the smallest particle diameter they were able to measure was $0.01\text{ }\mu\text{m}$.

This disparity between theoretical and experimental nucleation particle diameters makes it difficult to determine reasonable values for the nucleation (critical cluster) size of a particle in our simulations. Using classical nucleation theory (Seinfeld, 1986), we calculated the critical cluster size for nopinone (a terpene reaction product) and found the critical cluster diameter dp^* to be $0.002\text{ }\mu\text{m}$. To check the sensitivity of the MAEROS results to nucleation particle size we ran simulations for several nucleation particle sizes. As is shown in Table 2.4, the choice of nucleation size had a large effect on the system number concentration but a small effect on the system mass concentration. The reason for this is suggested in Figure 2.8a which compares the NP organic mass distribution with three simulated distributions differing only in the diameter chosen for the nucleation particle. As critical diameter for particle nucleation becomes smaller, the particle number concentration increases. For an assumed

nucleation diameter of $dp^* = 0.001 \mu\text{m}$ a smooth nucleation peak evolves during the 4 hour simulation. This simulated peak matches the shape of the NP observations, but it is centered at $0.004 \mu\text{m}$, 7.5 times smaller than the observed nucleation peak diameter of $0.03 \mu\text{m}$. As the assumed nucleation diameter is increased, the mean diameter of the simulated nucleation peak after 4 hours likewise increases. For $dp^* = 0.004 \mu\text{m}$, the simulated nucleation peak was centered at $0.005 \mu\text{m}$ after the 4 hour simulation. For larger assumed nucleation diameters ($0.014 \mu\text{m}$ and $0.029 \mu\text{m}$) neither coagulation nor condensation were effective in causing the particles to grow from the assumed nucleation diameter, and thus the nucleation aerosol peak remained where it was injected into the size distribution.

2.5.5 Saturation vapor pressure

The literature contains saturation vapor pressures for some atmospherically relevant primary organics (e.g. Stern et al., 1987; Pandis et al., 1991; Gill et al., 1983), but in this study we were interested in the behavior of the oxidation reaction products (ORPs) of the primary organics. ORPs are vapor phase aerosol precursors because of their low saturation vapor pressures. While the physical properties of these compounds are not well characterized, aerosol precursors are generally reported to have saturation vapor pressures between 0.001 and 1 ppbv (Pandis et al., 1992). We assessed the influence of vapor pressure over this range, both on the organic source rate required to simulate the observed data and on the resulting mass and number concentration of the size distribution.

The effects of saturation vapor pressure on the mass and number concentration are shown in Figure 2.9a. In Figure 2.9a particle number and mass concentrations are seen to decrease with increasing saturation vapor pressure. Number concentration decreases much more rapidly than mass concentration (note the log scale) because condensation occurs more rapidly than nucleation, leading to lower saturation ratios. In order for nucleation to occur a minimum saturation ratio is required but may not be attained if condensational processes are scavenging vapor. The number concentration depends on what type of gas-to-particle conversion (condensation or nucleation) takes place - which is controlled by the accommodation coefficient (as discussed above). We see that as the saturation vapor pressure of the organic approaches $1\text{e-}10 \text{ kg/m}^3$ (0.018 ppbv) nucleation is inhibited and fewer particles are generated. Table 2.4 shows that small changes in saturation vapor pressure ($\pm 10\%$) have little influence on the mass concentration of the system but a strong influence on the number concentration. Figure 2.9b shows that as the saturation vapor pressure of organic increases, the source emission rate of the organic must also increase in order to simulate a desired mass concentration. However, at high saturation vapor pressures, condensation becomes rapid enough that the source emission rates needed to achieve the organic mass observed by NP drop off. (This is evident in line A of Figure 2.9b) At these high vapor pressures, however, condensation onto existing particles dominates and no nucleation occurs.

2.5.6 Saturation ratio

In our simulations a saturation ratio of approximately 15 was needed to produce significant amounts of particles from a surrogate terpene oxidation reaction product vapor. It is difficult to compare this number with saturation ratios reported in the literature because the literature studies report nucleation events in terms of the amount of terpene reacted rather than in terms of the amount of condensible terpene oxidation product produced (Pandis et al., 1991). If we use the aerosol yields and nucleation threshold concentrations of terpene reported by Pandis et al. (1991), respectively 0.1 - 8.0% and 30-50 ppbv, to estimate the concentration of oxidation product, we get a concentration range between 0.03 and 4 ppbv. This is equivalent to a range of saturation ratios between 3 and 400 if p_{org} is 0.01 ppbv, as is our base case. Our simulated saturation ratio falls within this (admittedly large) range of saturation ratios.

2.5.7 Surface tension

The assumed surface tension, σ , of organic in this study was 25 dynes/cm. This is a typical value for organics. Stern et al. (1987) used a value of 30 dynes/cm, while Seinfeld (1986) lists values between 22 and 31 dynes/cm for different organic species. Nucleation rate, J , is highly sensitive to surface tension, as there is a σ^3 dependence in the exponent of Equation 2.1. Figure 2.10 shows that small changes in surface tension of the organic can lead to large changes in particle number concentration and significant changes in mass concentration. This means that the source rate of organic into the air parcel necessary to simulate the observed size distribution will vary depending on the surface tension assumed. As the surface tension increases, the source rate must increase for nucleation to occur. Table 2.4 indicates the strong influence of surface tension on particle formation in the system and shows the importance of further characterization of atmospheric organics.

2.5.8 Nucleation rate and NUCFLAG

The critical nucleation rate (the rate at which nucleation is considered to be significant) is generally accepted to be 1 particle/cm³-s (Pruppacher and Klett, 1978). In our simulations a rate of 1 particle/cm³-s was achieved at organic saturation ratios greater than approximately 16. This rate occurred during the last hour of the four hour simulation, as shown in Figure 2.11 and is a result of a gradual build up of organic vapor pressure due to the constant vapor flux. We also found that for the longer time simulations, while the maximum observed nucleation rate was very low (0.026/cm³-s) a nucleation peak was still observed at the end of the simulation. The production rate of particles was very slow but there was enough time for significant production to occur.

In our case study simulating the Puerto Rico aerosol, we based our results are strictly on classical nucleation theory (Equation 2.1). The homogeneous nucleation rate predicted by classical nucleation theory may differ from experimental observations and from other theories by up to 18 orders of magnitude (Springer, 1978). Raes and Van Dingenen (1992) suggest multiplying calculated nucleation rates by a 'nucleation tuner' between 10^4 and 10^6 based on their experimental results and calculated nucleation rates. We therefore investigated the influence on total mass and number concentrations of a variation of over three orders of magnitude in nucleation rate. Thus, the nucleation rate calculated in Equation 2.1 was multiplied by a constant in MAEROS (nucflag) effectively inhibiting or enhancing the nucleation process. Figure 2.12 shows that nucleation was inhibited for values of nucflag less than or equal to 0.1 and the mass concentration in this case changed solely by condensation of organic vapor onto existing aerosol. Values of nucflag greater than 0.1 enhanced nucleation, increasing the particle number concentration. However, coagulation of the additional nucleation particles had a limiting effect on the final observed number concentration. Mass increased with nucflag greater than 0.1 because of the increased surface area available for condensation.

2.5.9 Comments on sensitivity study

Results of this sensitivity study are summarized in Table 2.4. The parameter variations studied here put into perspective the influence each parameter has on the final mass and number size distributions. This insight enables us to identify parameters for which accuracy is essential in this type of modelling simulation. Table 2.4 shows that number concentration (and thus nucleation) is more sensitive to changes in model parameters than mass concentration. For example, the measured surface tension of organics falls in a fairly small range ~20-30 dyne/cm; however, a slight shift in the value of surface tension (e.g. from 25 to 27 dynes/cm) can determine whether new particles are formed (this depends on other parameters values also, of course). These sensitivity studies also demonstrate the co-varying nature of the input parameters. For example, the larger the assumed organic saturation vapor pressure, the larger the source rate must be to initiate nucleation. However, with more organic vapor available, the accommodation coefficient must be lowered in order to obtain condensational growth at a level compatible with simulating the observed size distribution.

From Table 2.4 it appears that choosing an appropriate mixing height is critical when modelling gas-to-particle conversion in the atmosphere; however, for specific sites and dates this is easily obtainable information and thus does not have to be a large source of uncertainty in models. Table 2.4 shows that the choice of critical nucleation diameter has a very large impact on the number and mass concentrations simulated. The critical nucleation diameter used in these simulations ($0.03 \mu\text{m}$) was a factor of 15 larger than the diameter calculated using homogeneous, homomolecular classical nucleation

theory. Such a disparity suggests two avenues of research: first, the calculation of critical diameter uses parameters (e.g., surface tension and vapor pressure) that are not well-known - laboratory studies are necessary to characterize atmospherically relevant organics. Second, in-depth investigations (both theoretical and experimental) of organic gas-to-particle conversion need to be continued, with a focus on atmospherically relevant results. In particular, studies on the applicability of homogeneous, homomolecular nucleation of organics to atmospheric systems are merited. These sensitivity studies also show that, in addition to being used to calculate the critical nucleation diameter, the physical organic parameters needed for modelling gas-to-particle conversion (e.g., surface tension and vapor pressure) can also be a large source of uncertainty in modelling number and mass concentrations.

The importance of determining these parameters more accurately is demonstrated by considering the influence that small percentage changes in CCN concentrations can have on global climate change. Charlson et al. (1987) in their classic review article relating oceanic phytoplankton to cloud albedo and climate made simple calculations showing that a 30% increase in CCN concentration could lead to a 1.3 K average global temperature decrease.

2.6 CONCLUSIONS

We used a modified version of the MAEROS code to simulate the evolution of a marine aerosol size distribution. The simulations describe a general approach for use in determining potential sources of observed nucleation-sized organic aerosol. Although fairly good matches between the observed and simulated data for the two scenarios (forest and ocean) were achieved, closer inspection of the input parameters eliminated the ocean as a source of organic aerosol. The ocean seems an unlikely source of nucleation particles because observed ocean organic fluxes are much smaller than the flux required by our simulations. Thus our simulations indicate that the most probable source of the observed organic nucleation particles is gas-to-particle conversion of organic vapors emitted from the forest. Our assumed forest source fluxes are very close to those reported in the literature.

This study also demonstrates the sensitivity of predicted number concentration to assumed input parameters. It is quite obvious that considerable experimental work needs to be done to obtain these necessary organic parameters. In 1977 Heisler and Friedlander cited the need to determine many organic parameters in order to model gas-to-particle conversion. The parameters needed were: gaseous diffusion coefficients, vapor pressures, density, solubility, activity coefficients and surface tension. Work in these areas is still necessary. Other information which would improve modelling of atmospheric aerosol evolution includes: measurements of accommodation coefficients for a variety of atmospherically relevant species, vertical profiles of atmospheric constituents, homogeneity of the air parcel, organic speciation and the interplay amongst different organics and other atmospheric vapors.

2.7 TABLES AND FIGURES

Table 2.1a General characteristics of the April 9/10/11 data set ($0.03 \mu\text{m} < dp < 10 \mu\text{m}$).

	OBSERVED		30 section representation	
	mass ng/m^3	number $(1/\text{cm}^3)$	mass ng/m^3	number $(1/\text{cm}^3)$
(1) SO_4	1362	462	1340	353
(2) Organic	628	1827	723	1639
Total (1+2)	1980	2289	2063	1992
CN measured w/CNC	1900/ cm^3			

*Note on observed data: CN number and SO_4 and Organic mass concentrations were measured; SO_4 , Organic, and Total number concentrations are result of data inversion calculations.

Table 2.1b 30 section representation of observed size distribution ($0.03 \mu\text{m} < dp < 1 \mu\text{m}$).

	mass (ng/m^3)	number ($1/\text{cm}^3$)
(1) SO_4	1233	353
(2) Organic	475	1639
Total (1+2)	1708	1992

Table 2.1c Characteristics of assumed initial size distribution compared with remote marine size distributions reported in the literature ($dp < 1.0 \mu\text{m}$).

	mass (ng/m^3)	number ($1/\text{cm}^3$)	site/reference
n.s.s. SO_4	960	430	assumed initial/this paper
Organic	570	165	assumed initial/this paper
n.s.s. SO_4	550-1500 2000-4000	250-590 150-300	NE Pacific/Quinn et al., 1993 Tropical Atlantic and Pacific/Hoppel et al, 1986
Organic	740-1200 820 530-740 200-400	- - - -	Enewetak/Chesselet et al., 1981 Various marine sites/Cachier et al., 1986 Tasmania/Eichman et al., 1980 Various marine sites/Hoffman and Duce, 1977

Note: n.s.s SO_4 stands for non sea salt SO_4

Table 2.2 Estimated emission rates for particles with $dp > 1.0 \mu\text{m}$ needed for MAEROS simulations to match observations.

simulation	organic (dp)	sulfate (dp)
FOREST (mh = 1000 m)	$3\text{e-}14 \text{ kg/m}^3\text{-s}$ ($2.7 \mu\text{m}$)	$2\text{e-}14 \text{ kg/m}^3\text{-s}$ ($5.5 \mu\text{m}$)
OCEAN (mh = 500 m)	$1.5\text{e-}14 \text{ kg/m}^3\text{-s}$ ($3 \mu\text{m}$)	$1\text{e-}14 \text{ kg/m}^3\text{-s}$ ($5.5 \mu\text{m}$)

Note: mh stands for mixing height.

Table 2.3 Forest and ocean scenario simulated organic vapor fluxes and simulation results.

simulation	organic vapor flux	accommodation coefficient	final mass* (kg/m^3)	final number* ($1/\text{cm}^3$)
FOREST				
4 h	$7.4\text{e-}11 \text{ kg/s-m}^2$	0.0105	$1.71\text{e-}9$	2007
10 h	$3.0\text{e-}11 \text{ kg/s-m}^2$	0.0065	$1.71\text{e-}9$	2005
OCEAN				
240 h	$3.2\text{e-}12 \text{ kg/s-m}^2$	0.00046	$1.71\text{e-}9$	1980

* $dp < 1.0 \mu\text{m}$

Table 2.4 Parameter variation for 4 h forest scenario showing effect on total mass and number concentration (organic + sulfate).

	base case	number test value	mass kg/m ³ (%)	total dp>0.1 um (1/cm ³) (%)	
Base Case results	-	-	1.71e-9 (0)	1992 (0)	146 (0)
mixing height (m)	1000	500	2.80e-9 (63)	3.3e4 (1540)	160 (9.7)
		1500	1.61e-9 (-5.8)	587 (-71)	139 (-4.5)
particle density (kg/m ³)	1500	1300	1.73e-9 (1.2)	1941 (-3.3)	
		1700	1.69e-9 (-1.2)	2029 (1.1)	
accom. coeff.	0.0105	0.005	1.67e-9 (-2.3)	3582 (78)	
		0.05	2.02e-9 (18)	587 (-71)	
dp* (um)	0.03	0.001	1.73e-9 (1.2)	4.9e6 (2.4e5)	
		0.004	1.72e-9 (0.6)	3.3e5 (1.6e4)	
		0.014	1.71e-9 (0)	1.2e4 (500)	
saturation vapor pressure (kg/m ³) (ppbv)	5.5e-11 (0.01)	5e-11 (0.009)	1.75e-9 (2.3)	4530 (126)	
		6e-11 (0.011)	1.69e-9 (-1.2)	961 (-52)	
surface tension (dyne/cm)	25	23	1.91e-9 (11.7)	1.1e4 (448)	
		27	1.68e-9 (-1.8)	596 (-70)	
NUCFLAG	1.0	0.001	1.68e-9 (-1.8)	589 (-71)	
		0.1	1.68e-9 (-1.8)	768 (-62)	
		10	1.78e-9 (4.1)	5852 (192)	
		1000	1.96e-9 (14.6)	1.3e4 (548)	

Note: % = ((test - base)/base)*100

Figure 2.1a Twomey inversions (with which simulation results were compared) and initial organic and sulfate mass distributions used in these simulations. a) organic (4/10-11/92).

Figure 2.1b. Twomey inversions (with which simulation results were compared) and initial organic and sulfate mass distributions used in these simulations. b) sulfate (4/9/92).

Figure 2.2a Comparison of initial mass distributions for organics assumed in simulation work (converted to 5-section distributions) with remote marine mass distributions reported in the literature.

Figure 2.2b Comparison of initial mass distribution for sulfate assumed in simulation work with remote marine mass distributions reported in the literature.

Figure 2.3 Air parcel back trajectory (from J. Merrill) showing the lack of continental influence on the air parcel for upwards of 10 days

Figure 2.4 Schematics of air parcel inputs during a) forest scenario, b) ocean scenario.

Figure 2.5a Organic mass distribution calculated for the forest scenario compared to assumed initial and observed distributions ($t = 4\text{h}$).

Figure 2.5b Organic mass distribution calculated for the forest scenario compared to assumed initial and observed distributions ($t = 10\text{h}$).

Figure 2.6 Organic mass distribution calculated by MAEROS for the ocean scenario compared to assumed initial and observed distributions.

Figure 2.7 Lines of constant organic vapor source rate showing the relationship between mass and number concentration and accommodation coefficient (for 4h forest scenario).

Figure 2.8 Organic mass distributions as a function of nucleation diameter for $t = 4\text{h}$.

Figure 2.9a Influence of organic saturation vapor pressure on simulated mass and number concentration (for 4h forest scenario).

Figure 2.9b Lines of constant system mass as a function of organic saturation vapor pressure and organic vapor source rate (for 4h forest scenario).

Figure 2.10 Influence of surface tension on system mass and number concentration. Note log scale for number concentration (for 4h forest scenario).

Figure 2.11 Nucleation rate as a function of time (for 4h forest scenario).

Figure 2.12 Influence of nucleation rate variation on final system mass and number concentration. Note that nucleation is not observable until NUCFLAG > 0.1 (for 4h forest scenario).

2.8 REFERENCES

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CHAPTER 3

THE EFFECT OF SURFACTANT LAYERS ON THE SIZE CHANGES OF AEROSOL PARTICLES AS A FUNCTION OF RELATIVE HUMIDITY

3.1 ABSTRACT

We present water sorption/desorption curves for NaCl and carbon black particles associated with individual organic surfactants. The surfactants used in this study were Tween80 (a polyoxyethylene sorbitan ester and non-ionic surfactant), dodecyl sulfate-sodium salt (an anionic surfactant) and azelaic acid (an organic surfactant). The sorption curves show the change in mass of the particles as a function of relative humidity and were determined using an electrodynamic particle balance. Our results show that the presence of Tween80 on a NaCl particle lowers the deliquescence relative humidity from 75% for a pure NaCl particle to 70-73% depending on the amount of Tween80. Another effect of the Tween80 is a decrease in the maximum relative mass gain (M/M_0) at the deliquescence point. At equilibrium, M/M_0 ranges from 4.0 to 4.1 for the pure NaCl particle while M/M_0 for the Tween80/NaCl particles ranges between 1.75 and 3.5 again depending on the amount of Tween80. For the carbon black/surfactant systems our results suggest that while uncoated carbon black particles are hydrophobic, a surfactant coating on carbon black particles increases the hygroscopicity of the carbon black particles, even if the surfactant itself is hydrophobic. Carbon particles coated with Tween80 showed a relative mass gain of 1.2 at 90% relative humidity; carbon particles coated with dodecyl sulfate-sodium salt showed a relative mass gain of 1.1-1.2 at 90% relative humidity; and carbon particles coated with azelaic acid showed a relative mass gain of 1.4 at 86% relative humidity.

3.2 INTRODUCTION

In the last chapter we modelled the evolution of a population of particles composed of organics and sulfate, assuming several different initial conditions. The modelling did not, however, make any assumptions about the mixing state of the particles nor how the composition of the particles might influence particle behavior in the atmosphere. In this chapter we study how the composition of individual particles will influence their growth characteristics. Specifically, we experimentally investigate the effect an organic coating has on both salt (hygroscopic) particles and elemental (hydrophobic) particles. If we accept that the atmospheric aerosol, such as that studied in the previous chapter, is an internal mixture, the growth characteristics of the aerosol due to water uptake may differ significantly from an aerosol with the same mass composition that is an external mixture. Because water vapor scavenging by particles is the basic mechanism for cloud, ice, and fog formation, understanding compositional effects will enable us to better model the particles' roles in atmospheric processes such as visibility degradation and radiative scattering.

In recent years, a number of researchers have related atmospheric phenomena such as cloud formation and visibility degradation to the composition of atmospheric aerosol particles (e.g., Larson and Cass, 1989; Sloane, 1984; Rood et al., 1989; Novakov and Penner, 1993). This type of research presents challenges because the composition and structure of atmospheric particulate matter are not easily characterized, and the interactions between the aerosol particles and water vapor in the atmosphere are complex.

Ambient aerosol particles often consist of mixtures of organic and inorganic substances (McMurray and Stolzenburg, 1989; Appel et al., 1979), and it has been theorized that a possible structure for such particles is an aqueous or solid core with an organic outer coating (Podzimek and Saad, 1975). This is a reasonable possibility given that there exist many potential sources for organic coatings on atmospheric particles. For example, atmospheric aerosol particles composed of organics and aqueous solutions are produced when organic surface films on oceans and fresh waters are disrupted by bubble bursting mechanisms (Podzimek and Saad, 1975; Baier, 1972; Marty et al., 1979). Aerosol particles which pass over urban or agricultural areas can potentially become coated with the primary and secondary organics resulting from anthropogenic pollution and/or the waxy organics released by plants (Gagosian et al., 1981). During combustion processes organics are co-generated with elemental carbon particles, and the organics can adsorb onto the elemental carbon particles (Ogren and Charlson, 1983). The coating composition will affect particle behavior. Thus it is important to consider some typical families of organics which may serve as coatings for atmospheric aerosol particles include carboxylic acids, alcohols, esters, and aldehydes (Gill et al., 1983). We focus specifically on the coatings that tend to be surface active (surfactant) in nature.

Some studies have shown that the presence of a surfactant coating on an aerosol particle may influence how a coated particle grows or evaporates in a humid environment. Chang and Hill (1980) studied the evaporation rate of water droplets falling in the presence of nonanal and nonanoic acid, products of the ozone-1-decene reaction. Their results imply that the evaporation rate of the water droplets decreases as a result of exposure to gaseous organics. Otani and Wang (1984) investigated the growth rate of NaCl solution droplets coated with monolayers of cetyl alcohol, a surfactant. They found that a surfactant coating reduces the growth rate of the NaCl droplets, although with additional time the surfactant-coated droplets grew to the same size as the uncoated droplets. Both of these studies considered multi-particle systems and were, therefore, unable to follow an individual particle as it was exposed to different conditions.

Individual liquid droplets and the limiting effect of an organic layer on the evaporation kinetics have been investigated in electrodynamic balances. Snead and Zung (1968) studied coated and uncoated water

droplets and ethylene glycol droplets using an electrodynamic particle balance. They found that water droplets coated with n-decanol evaporate two orders of magnitude slower than uncoated water droplets. Ethylene glycol droplets coated with n-dibutylphthalate evaporate three to four times slower than uncoated ethylene glycol droplets; the relatively low reduction in evaporation rates probably results when the droplets are not completely coated. Rubel and Gentry (1984) investigated slightly acidic water drops coated to different degrees with hexadecanol. For the water/hexadecanol system, they found that water droplets having a surface coverage of greater than 97.5% have evaporation and condensation rates decreased by one to two orders of magnitude beyond what is observed for water droplets with less coverage.

These single particle results are consistent with earlier studies evaluating the limiting effect of organic layers on gas transport through flat, gas surfaces. For example, Langmuir and Langmuir (1927) studied the effect of surfactant coatings on the evaporation rate of water and ethyl ether solutions. They found that a cetyl alcohol layer on a shallow pool of water slows the water evaporation rate by 50%. In later work Langmuir and Schaefer (1943) developed a method for measuring the permeability of various surfactant monolayers to gases on a flat water surface. They found that longer chain lengths and higher surface density of the organic surfactant increases the ability of the surfactant to inhibit evaporation. Other studies (Plevan and Quinn, 1966; Sada and Himmelblau, 1967) also show that the presence of an organic layer reduces the transfer rate of a gas through an organic layer into a quiescent liquid. These studies show that the physical properties of the organic and the amount of surface coverage by the organic are major factors in reducing gas transfer.

The investigations discussed above indicate that organic layers slow water vapor transport. There is some evidence, however, that the presence of an organic layer on a hydrophobic core particle, such as elemental carbon (EC), may actually increase water sorption and cause a coated, originally hydrophobic particle to grow as the particle is exposed to high relative humidities in the atmosphere. For example, Dasch and Cadle (1989) noted that particles with high ratios of organic carbon (OC) to EC were preferentially removed by precipitation. Ogren and Charlson (1983) reported that elemental carbon particles would not sorb water but adsorbed other compounds (e.g., sulfuric acid) and could through adsorption become hygroscopic. Since surfactant molecules have both a hydrophilic and hydrophobic part, it is possible that under certain orientations, a layer of surfactant molecules may increase the hygroscopicity of an aerosol particle.

The purpose of this research is to investigate how individual aerosol particles coated with an organic layer interact with a humid environment. Other studies found in the literature concerning growth of layered aerosol particles focus on particles with liquid cores. Here we extend previous research by

investigating water uptake by both coated aqueous solution droplets and by coated insoluble carbon black particles (a surrogate for atmospheric EC particles). We present results for the uptake and release of water vapor by these particles. We have compared the water sorption/desorption curves for particles of differing composition to investigate composition-dependent particle growth. (These curves show how a particle changes size or mass as a function of the relative humidity of the surrounding gaseous environment.) The exact form of the curves depends on the particle composition, including whether the particle is deliquescent or hygroscopic and non-deliquescent.

A dry, deliquescent particle exposed to increasing relative humidity will maintain its dry weight until the humidity surrounding the particle is equal to the particle's deliquescent humidity. At the deliquescent humidity the particle experiences a sudden increase in mass due to the condensation of water on its surface and subsequent change from a solid particle to a solution droplet. As the humidity increases past the particle's deliquescent point, the liquified particle will continue to grow, but at a much slower rate. A deliquesced particle exposed to a decreasing relative humidity scan does not abruptly shrink back down to its dry mass at the deliquescent humidity; rather, a hysteresis effect occurs where the particle gradually loses mass until, at a relative humidity substantially lower than the deliquescent humidity, the droplet crystallizes. Crystallization occurs rather suddenly and the droplet mass returns to the original dry mass of the particle (Tang and Munkelwitz, 1984). This type of particle growth is observed for deliquescent salts such as NaCl and $(\text{NH}_4)_2\text{SO}_4$.

Orr et al. (1958) offer a physical explanation for this sudden transition of the particle from solid to liquid phase. At relative humidities below the deliquescence relative humidity the particle will physically adsorb a very thin (order of nm) layer of water on its surface. This water layer is saturated with respect to the solid particle. At the deliquescence relative humidity an unstable situation is created where the solid particle dissolves into the water layer lowering the vapor pressure over the surface of the particle. In accordance with Raoult's Law, the lower vapor pressure causes more water to condense onto the particle which in turn causes more of the particle to dissolve into the liquid layer to maintain equilibrium between solid and liquid phase of the particle. This cycle continues until the solid particle is completely dissolved.

Differences in hygroscopicity of particles due to differences in the particles' compositions can be determined by comparing the hysteresis curves of the different particles. A more hygroscopic particle will exist as a solution droplet over a greater range of humidities than a less hygroscopic particle and/or the hygroscopic particle will be able to retain more water over this humidity range.

A hygroscopic, non-deliquescent particle will also increase in mass as water sorbs onto its surface

during conditions of increasing relative humidity. In contrast to deliquescent particle growth, however, no sudden change in mass is observed for hygroscopic non-deliquescent particles. As the relative humidity is decreased the particle will gradually lose the water it has taken up. The particle mass will decrease along the same path as it increased.

3.3 EXPERIMENTAL METHOD

3.3.1 Apparatus

In the past two decades, the electrodynamic balance has become an increasingly popular tool for the study of single particle systems. Because of the versatility inherent in the balance, researchers have been able to investigate topics ranging from superconductivity (Grader et al., 1989) to light-scattering (Schweiger, 1990) to soil characteristics (Tognotti et al., 1991). The basic theory of the electrodynamic balance has been fully described elsewhere (Davis, 1987) so only a brief description is given here.

An electrodynamic particle balance suspends a single, charged particle in an electric field within a controlled gaseous environment. The balance consists a central ring electrode situated halfway between two endcap electrodes. A dc voltage is applied across the balance's endcap electrodes, and the resulting electric field is used to counteract the force of gravity on the particle. Using the dc voltage, the particle can be vertically centered within the balance chamber. An ac voltage is applied to the ring electrode and is used to horizontally center the suspended particle.

The force balance on a suspended particle can be written

$$mg = \frac{C_o q}{2z_o} V_{bal} \quad (3.1)$$

which can be rearranged to

$$\frac{m}{q} = \frac{C_o}{2gz_o} V_{bal} \quad (3.2)$$

where m is the mass of the particle; q is the charge on the particle; C_o is the balance calibration constant; V_{bal} is the dc balancing voltage across the endcap electrodes; g is the gravitational constant; and z_o is the distance between the center of the balance chamber and an endcap electrode. Equation 3.2

shows that the dc voltage needed to suspend a particle is inversely proportional to the charge to mass ratio, q/m , of the particle. Assuming the charge q on a particle remains constant, the relative changes in mass of a growing or shrinking particle can be determined from measurements of the relative changes in dc voltage V_{bal} needed to keep the particle balanced. The value of the balance calibration constant, C_o , is not needed for measurement of relative changes of mass. (Theoretical calculations have shown C_o to vary between 0.31 and 1.31 depending on balance geometry (Sloane and Elmoursi, 1989; Ataman and Hanson, 1982)). The ac voltage does not create a force component in the vertical direction. Thus, it has no effect on the vertical force balance (Equation 3.1).

The balance used in this experiment consists of two flat-plate, aluminum endcap electrodes and a cylindrical aluminum ring electrode. A cross section of an electrodynamic balance chamber is shown in Figure 3.1. PVC electrode holders serve as spacers to insulate the electrodes from the aluminum chamber housing the balance. Holes bored vertically through the top and bottom electrodes allow the introduction and removal of a gas stream of controlled relative humidity. The hole in the bottom electrode is 2.85 cm^2 . This hole is covered with a 30.5% open, stainless steel mesh. The ring electrode has four horizontal holes through it: two are used as laser ports, one is for viewing a suspended particle through a microscope objective and one hole is not used. The chamber walls have four glass-covered windows aligned with the holes in the ring electrode.

3.3.2 Generation of a controlled relative humidity gas stream

To develop water sorption/desorption curves (plots of relative particle mass versus relative humidity) with the data from the electrodynamic balance, it is necessary to be able to control the relative humidity within the balance chamber. In this study a gas stream was generated with known relative humidity by combining a dry air stream with an air stream close to saturation (Figure 3.2). The nearly saturated stream was obtained by passing a dry filtered air stream through a water bubbler. By varying the ratio of dry to saturated air in the combined air stream, controlled relative humidities in the range between 10 and 95% could be achieved. The wet and dry gas stream flows were controlled by Tylan mass flow controllers (Model FC-260). The relative humidity of the combined gas stream was determined using tabulated values for the vapor pressure of the gas as a function of dewpoint and dry bulb temperature. The dewpoint temperature of the combined stream was measured using two General Eastern dewpoint hygrometers (Model Hygro-M1): one placed at the inlet and one at the outlet of the balance chamber. To find the dewpoint temperature in the chamber an average of these hygrometer readings was used. Generally the dewpoint temperatures measured by the two hygrometers were within 0.4° C . The dry bulb temperature was measured with a digital temperature probe.

In the water sorption/desorption experiments, measurements of water uptake by the particle as a

function of relative humidity were made by exposing the particle to both increasing and decreasing step changes in relative humidity and allowing the particle to grow or shrink to equilibrium size at each step change in relative humidity. This series of step changes is referred to as a relative humidity scan. As the suspended particle grew or shrank in response to the relative humidity changes, changes in balancing voltage were recorded. From these data, the relative mass changes of a particle over a range of relative humidities were obtained and the sorption/desorption curves were plotted.

3.3.3 Experimental procedure

To suspend a particle in the balance chamber the dc voltage was set between 0 and 100 V dc and an ac voltage of approximately 2000 V ac was applied to the ring electrode in order to "trap" the particle in the potential well created by the ac field. Droplets were sprayed through the top electrode into the chamber using a small pump spray bottle to aerosolize a solution of the desired droplet composition. (The particles were charged through the spraying process by frictional charging.) Once a particle was caught in the ac field it was allowed to dry and the dc voltage across the endcap electrodes was adjusted until the particle was centered in the null point of the balance chamber. At this point the particle was held centered, and the dc voltage was recorded as the balancing voltage of the dry particle, V_{bal} .

Once a particle was balanced in the chamber, an air stream was introduced into the chamber through the bottom electrode (Figure 3.2). The flow rate of the gas stream was typically 150 cc/min and had a velocity of 0.032 m/s past the suspended particle which was enough to create a significant drag force on the particle. The drag force acted to lift the particle so that less voltage was required to suspend the particle at the balance's null point when the gas stream was flowing through the chamber. The force balance on the particle (Equation 3.1) must be rewritten to include drag force effects

$$mg = \frac{C_0 q}{2z_0} V_{bal,drag} + F_{drag}$$

3.3

where $V_{bal,drag}$ is the balancing voltage when the force of drag is acting on the particle and F_{drag} is the drag force. Equation 3 can be written solely as a function of the mass of a suspended particle by substituting in for q using Equation 3.1; using Stoke's Law, ($F_{drag} = 6\pi r\mu U$ for a spherical particle where r is the radius of the particle, μ is the viscosity of the gas flowing past the particle, and U is the velocity of the gas stream); and using the fact that the mass of a spherical particle is given by $(4\pi/3)r^3\rho$ (ρ is the density of the particle).

$$mg = \frac{C_o q}{2z_o} V_{\text{bal,drag}} + 6\pi\mu U \left(\frac{3}{4\pi\rho} m \right)^{\frac{1}{3}} \quad 3.4$$

Equation 3.4 is based on several assumptions. Because Stoke's Law was used in the derivation of Equation 3.4 and Stoke's Law assumes a spherical particle, Equation 3.4 is valid for spherical particles. In Equation 3.4, we used Stoke's Law to calculate the drag force on a particle since the calculated particle Reynold's number is less than 1.0, i.e., in the laminar flow region. The particle Reynold's number was found using: $Rep = (\rho_g d_p U)/\mu$ where ρ_g is the density of the gas, d_p is the particle diameter, U is the gas velocity, and μ is the viscosity of the gas. For a typical particle in these experiments with a diameter of 30 μm (estimated using the calibrated microscope eyepiece) a particle Reynold's number of 0.06 was found ($U = 0.032 \text{ m/s}$, $\rho_g = 1.2 \text{ kg/m}^3$ and $m = 1.85 \times 10^{-5} \text{ kg/m-s}$). This is well within the laminar region, and thus, in this study, Equation 3.4 was assumed to hold.

The velocity at the null point of the chamber (i.e., the velocity of gas past a suspended particle) was experimentally measured using polystyrene latex spheres of known size and density. An individual sphere was suspended in the chamber, and the balancing voltage at different flow rates (corresponding to different velocities) was recorded. Using Equation 3.4 with the known mass and density and measured $V_{\text{bal,drag}}/V_{\text{bal}}$, the velocity past the particle, U , is determined for each flow rate. The velocity was calculated to be 0.032 m/s for a flow rate of 150 cc/min.

Equation 3.4 can be used iteratively to determine the dry mass of the particle suspended in the balance chamber. As the suspended particle is exposed to a gas stream of increasing relative humidity and sorbs water, further corrections must be made to Equation 3.4 to account for changes in particle density. In this research, it was assumed that a suspended particle accumulating water could be modeled as two concentric spheres. The inner sphere represents the original particle and the outer sphere represents a layer of water around the particle. (For particles coated with an organic layer, it was assumed that the organic layer had a negligible effect on the density and mass of the core particle.) Using this layered sphere model, overall particle density can be determined as a function of the mass and density of the separate components. The equation for overall particle density as water sorbs onto the particle can then be expressed as

$$\rho = m \left(\frac{m - m_p}{\rho_w} + \frac{m_p}{\rho_p} \right)^{-1} \quad 3.5$$

where ρ is the total particle density; m is the total particle mass; m_p is the mass of the core particle; ρ_w is the density of water; and ρ_p is the density of the dry core particle. A similar approach was used by Tang and Munkelwitz (1977). Substituting Equation 3.5 into Equation 3.4 and simplifying one obtains:

$$m = m_p \frac{V_{\text{bal,drag}}}{V_{\text{bal}}} + \frac{6\pi\mu U}{g} \left(\frac{3}{4\pi} \right)^{\frac{1}{3}} \left(\frac{m}{\rho_w} + \frac{m_p(\rho_w - \rho_p)}{\rho_w \rho_p} \right)^{\frac{1}{3}} \quad 3.6$$

As the dry bulb temperature in these experiments ranged only between 20 and 25° C, the values of ρ_w and m in Equations 3.4 - 3.6 were assumed to be invariant with temperature. This assumption induces an error of less than 2% for the value of m and 0.3% in ρ_w . The assumed values for these variables were $m = 1.85 \times 10^{-5}$ kg/m-s (Wark and Warner, 1981), $\rho_p = 1950$ kg/m³ for carbon black, $\rho_p = 2165$ kg/m³ for NaCl, and $\rho_w = 1000$ kg/m³ for water (Weast, 1980).

3.4 RESULTS AND DISCUSSION

The dc voltage required to balance a particle in the electrodynamic balance chamber was recorded as a function of increasing and decreasing relative humidity. The relative mass gain of the particle was calculated using Equations 3.4 and 3.6 to convert dc balancing voltage to particle mass as discussed above. Individual particles composed of NaCl, carbon black (Degussa Corp., N-550), Tween80 (a non-ionic organic surfactant), dodecyl sulfate, sodium salt (DDS, an anionic organic surfactant), azelaic acid (an organic surfactant), and NaCl and carbon black particles coated with different amounts of the individual surfactants were studied. The actual extent of surfactant coating on individual particles is not known quantitatively. Thus, the observed changes in deliquescence relative humidity and relative mass can only be interpreted qualitatively.

3.4.1 Balance performance and data consistency

To characterize the balance, prior to performing water sorption experiments for surfactant and surfactant-coated particles, the balance was used to develop a water sorption curve for a NaCl particle. The response of NaCl to relative humidity changes is well characterized (Tang and Munkelwitz, 1977, Cohen et al., 1987) and serves as a check on balance operation. As the suspended NaCl particle changed from a dry crystal to a highly concentrated saline droplet during deliquescence, the optical appearance of the particle, as viewed through the microscope objective, changed from that of a clearly irregularly-shaped particle to a spherical droplet. Table 3.1 compares our experimental results for maximum relative mass gain at the deliquescence relative humidity, deliquescence relative humidity,

and crystallization relative humidity for NaCl particles with those found in the literature. These data for NaCl agree with predicted and experimental results for the deliquescence relative humidity and relative mass gain presented in the literature by Tang and Munkelwitz (1977), Cohen et al. (1987), McMurray and Stolzenburg (1989) and Winkler (1973). This agreement indicates that the balance system is performing properly and provides a measure of confidence in the experimental results. The crystallization relative humidity of NaCl observed in these experiments (49% - 54%) was somewhat higher than the range of crystallization humidities (39.5% - 45%) reported in the literature.

Data consistency was checked in several ways: comparing water sorption curves for different particles of the same composition, water sorption measurements for particles injected into the balance by different methods, and repeated water sorption measurements on the same particle (Figure 3.3). These comparisons show good reproducibility of the data. For example, Figure 3.3a shows curves from two different carbon black particles coated in 0.01 M Tween80. The coated particles were obtained by aerosolizing a solution composed of 0.01 M Tween and carbon black and allowing the resulting particles to dry. These curves demonstrate that experimental results are reproducible to within a few percent. In our experiments particles were to be injected into the balance in both wet (i.e., in a water mixture) and dry forms. Wet particles were sprayed in as solution drops and allowed to dry before beginning a relative humidity scan. Dry particles were injected in powdered form. Thus it is important to compare results from these two injection methods. Figure 3.3b shows water sorption curves for DDS particles, one which was initially wet and the other dry. The injection method used did not appear to significantly influence the water sorption ability of the DDS particles.

In Figure 3.3c repeated humidity scans on the same carbon black particle coated in 0.01 M Tween80 showed good agreement to within 2-3%. Although the sorption profile appears to follow the same path on both humidity scans the relative mass ratio of the dry particle was slightly greater than one at the start of the second scan, i.e., a larger balancing voltage was required to suspend the particle at the end of the run than had been required to suspend the dry particle at the beginning of the run. This increase in mass was occasionally observed at the end of humidity scans on some particles. This could be because some of the water sorbed during the first run may not have completely desorbed or because the particle was losing charge and required more voltage to balance it. The second explanation seems unlikely as particles have been balanced in the chamber for a week or longer with no noticeable loss of charge.

3.4.2 Effects of a surfactant coating on a deliquescent particle

For the NaCl/Tween80/water system several characteristics were observed which have also been noted in other experiments studying the effects of organic layers on liquid drops, e.g., Winkler and Junge

(1972). Figure 3.4 compares the hysteresis curves of several individual NaCl particles coated with different amounts of Tween80. These particles were generated from aqueous solutions composed of varying amounts of Tween80 and NaCl dissolved in water. Following injection the liquid particles were dried, then exposed to increasing and decreasing relative humidity. As it was not possible to quantify the relative amount of Tween80 and NaCl in each particle a ratio based on the relative amounts of Tween80 and NaCl in the bulk solution was used to differentiate the particles. The maximum relative mass gain observed for the particles at deliquescence decreased as the NaCl/Tween80 ratio decreased. An uncoated NaCl particle had a maximum relative mass gain of 4.1 while the particle with a "medium" NaCl/Tween80 molar ratio (5 moles NaCl/mole Tween80) had a maximum relative mass gain of 3.5 and the particle with the "low" NaCl/Tween80 molar ratio (3 moles NaCl/mole Tween80) showed a maximum relative mass gain of 1.8. This difference in the maximum relative mass gain for coated and uncoated NaCl particles implies that the organic coating limits the total amount of water a particle can sorb. This conclusion, however, is based on the assumption that the mass of the surfactant coating is negligible. In the case of the particle with the "low" NaCl/Tween80 ratio such an assumption may not be valid. Figure 3.4 also shows that the deliquescence point of the coated particles was not as sharply defined as the deliquescence point of the uncoated NaCl particle. Winkler and Junge (1972) noted in their *in situ* study of atmospheric aerosols that multi-component particles deliquesced more smoothly than single component particles.

Figure 3.4 also illustrates that the surfactant coating on a salt particle lowers the deliquescent relative humidity of the particle. The particle with the "low" NaCl/Tween80 ratio deliquesced at a relative humidity of 71%, the particle with the "medium" NaCl/Tween80 ratio deliquesced at 73% and the uncoated NaCl particle deliquesced at 75% relative humidity. Although it seems intuitive that a coating which inhibits the uptake of water should shift the deliquescence point to a higher relative humidity the opposite effect was observed. A possible reason for this is discussed below.

The relative humidity at which deliquescence occurs is a function of the activity of the solute in solution. Orr et al. (1958) show that for a single component particle the deliquescence humidity decreases as the activity of the solute increases. They showed the solute activity to be a function of the surface energy of the particle and the particle radius. In the experiments presented here, the particles studied are large enough that the radius of the particle is not a factor in the solute activity equation. However, the addition of a surfactant may affect the surface energy of the NaCl particle resulting in an increase in solute activity which would correspond to a decrease in deliquescence relative humidity. Wexler and Seinfeld (1991) have theoretically shown that the deliquescence relative humidity in a multi-component, internally mixed aerosol is lower than that of the individual deliquescence points of components contained in the aerosol. The proof, which relies on thermodynamic equilibrium

assumptions, is consistent with the observed decrease in deliquescence relative humidity for the NaCl/Tween80 system. A summary of the results for the NaCl/Tween80 system is given in Table 3.2.

As the thickness of the Tween80 coating increased so did the time required for the particle to grow to equilibrium size in the balance system. An uncoated NaCl particle required 7 minutes at 75% deliquescence relative humidity to grow to equilibrium size. A NaCl particle with a "medium" NaCl/Tween80 ratio required 30 minutes to reach equilibrium size at 73% relative humidity, while a NaCl particle with a "low" NaCl/Tween80 ratio required 90 minutes to reach equilibrium size at a relative humidity of 71%. This time difference indicates that the surfactant coating is affecting the surface kinetics of the growing NaCl particle. Otani and Wang (1984) observed similar decreases in adsorption rates for coated NaCl droplets. Their results show that a coated saline drop takes two to six times longer to grow to equilibrium size at 99.5% relative humidity than an uncoated droplet. Otani and Wang's study did not observe the final decrease in growth of the particle that was seen in our experiments. Podzimek and Saad (1975), however using a one-dimensional cloud model, predicted decreases in particle growth for salt nuclei covered by a layer of cetyl alcohol. However, part of the decrease in relative mass gain observed in our experiments may be attributed to our assumption of negligible surfactant mass.

3.4.3 Effects of a surfactant coating on a non-deliquescent particle

Our studies of the effects of surfactant coatings on vapor uptake by liquid particles are consistent with the effects reported in the literature, providing confirmation of our approach and results. Thus, we now shift the discussion to our experiments studying water sorption by uncoated carbon black particles and by carbon black particles coated with organic surfactants. Figure 3.5 shows the results of exposing an uncoated carbon particle to environments of increasing and decreasing relative humidities. The carbon black appears to be hydrophobic as there is no noticeable uptake of water by the particle for relative humidity ranging from 15 to 85%. The hydrophobicity of elemental carbon particles has also been well established by other researchers. However, Ogren and Charlson (1983) reported that elemental carbon particles would not sorb water but adsorbed other compounds (e.g., sulfuric acid) and could through adsorption become hygroscopic. This suggests that any observed changes in the hydration properties of the coated carbon black particles will be attributable to the presence of other compounds on the particle surface.

Figure 3.6 compares the water uptake profiles for a Tween80 particle and a carbon black particle coated with Tween80. A Tween80 particle exhibits a relative mass gain of 1.5% at 80% relative humidity while carbon black particles coated in 0.01 M Tween80 exhibit a relative mass gain of 1.13 at 80%

relative humidity; the existence of the organic surfactant coating on the particle making the particle hygroscopic. The shape of the hygroscopicity curve for the coated carbon particle is similar to that of the hygroscopicity curve for Tween80. The water uptake profiles for individual particles of Tween80 and for carbon black coated with Tween80 exhibit a smooth, gradual uptake of water as the relative humidity to which the particle is exposed increases. The hysteresis phenomenon is not observed for particles of Tween80 and carbon black coated with Tween80 as water loss during decreasing relative humidity scans follows the same path as the water uptake for increasing relative humidity scans.

The presence of a DDS coating on carbon black also increases the hygroscopicity of the carbon black. In Figure 3.7 we compare the hygroscopicity curve for a DDS particle with that of a carbon particle coated in 0.01 M DDS. The coated carbon black particle sorbs water in the amount of 10 to 20% of the dry carbon particle mass. This result was unexpected following experiments with pure DDS particles which showed no tendency to sorb water. A hypothesis explaining this is that in the pure DDS particle the hydrophilic ends of the DDS cluster together so that the hydrophobic ends are outwards. Thus a water repellent surface is presented to the humid environment of the balance chamber. However, when mixed in solution with carbon black, a micelle-like phenomenon occurs, and the hydrophobic ends of DDS attach to the hydrophobic carbon leaving a hydrophilic surface outward for the water vapor in the balance chamber to sorb onto. Figure 3.7 also suggests that the DDS-coated carbon black particle does not lose water as readily as it sorbs water. For a given relative humidity, the relative mass of the DDS-coated particle is slightly greater during the decreasing relative humidity scan than during the increasing relative humidity scan.

The final phase of this study investigated the effect of azelaic acid coating on carbon black particles. Azelaic acid is a highly surface active compound which has been found in rain, snow and atmospheric aerosol particles (Lunde et al., 1977; Grosjean et al., 1978). Because azelaic acid has been detected in precipitation and atmospheric aerosols the behavior of this compound as a function of relative humidity is relevant for understanding atmospheric processes. Figure 3.8 shows the hygroscopicity curve for a carbon black particle coated in 0.01 M azelaic acid. We see similar water sorption profiles for this particle as for the carbon particle coated in Tween80 (Figure 3.6) in that we see a gradual uptake of water by the particles as the relative humidity increases. Similar to the pure DDS case, the pure azelaic acid does not appear to pick up any water when exposed to relative humidity of up to 86%. Potentially the micelle-like structure hypothesized for the DDS/carbon system forms for the azelaic acid/carbon system, as well.

Table 3.3 summarizes the results of the experiments studying the effect of surfactant coatings on water sorption by carbon black. The particle dry mass was calculated using Equations 3.5 and 3.7. The

maximum relative change in mass, $(M/M_o)_{\max}$, of the particle was taken to be maximum value of that quantity over a range of relative humidities on the sorption curves. The relative humidity at which $(M/M_o)_{\max}$ is observed is also noted. It can be seen from the Table 3.3 that, of the surfactants investigated, a coating of azelaic acid is most effective at increasing the hygroscopicity of the carbon black particle. The azelaic acid coating enabled the carbon particle to sorb water amounting to 40% of the particle's dry weight at 86% relative humidity. A coating of Tween80 on carbon also increased carbon particle hygroscopicity but not as much as is observed for the particle coated with azelaic acid. A carbon particle coated with Tween80 sorbed water amounting to 20% of the particle's dry weight at 90% relative humidity. A coating of DDS appeared to have less of an effect on the carbon particle's hygroscopicity than the other surfactants studied. A DDS coated carbon black particle sorbs water amounting to 10-20% of the particle's dry weight.

The relative mass gains observed in these experiments correspond to more than a monolayer of water adsorbed onto the coated carbon particle's surface and so cannot be solely explained by monolayer adsorption onto the hydrophilic ends of a micelle-like structure. For example, the relative mass gain observed for the DDS coated carbon particle is equivalent to the formation of a several micrometer thick layer of water on the particle. One simplifying assumption made at the beginning of the work was that the particles studied are solid spheres. The carbon particles are actually slightly porous with a surface area of $41 \text{ m}^2/\text{kg}$ (Degussa Corp., 1989). Calculations taking into account the actual particle surface area, however, still do not explain the relative mass gain solely in terms of a monolayer adsorption. Thus some phenomenon in addition to surface adsorption must be occurring.

The orientation and thickness of the adsorbed surfactant layer may play a key role in determining how much, and by what mechanism, water can be taken up by the particle. Diffusion of water vapor through the surfactant layer and enhanced hydrogen bonding sites for water molecules along the surfactant molecules are two possibilities which can influence the amount and distribution of the water on the carbon particle surface. Additionally, the presence of the surfactant layer with a sorbed water monolayer may cause a lowered equilibrium water vapor pressure over the particle's surface resulting in further condensation of water on the particle beyond the monolayer at humidities less than supersaturation.

3.4.4 Interpretations and implications

The results presented in this paper suggest various phenomena which may occur in the atmosphere when common atmospheric components such as water, elemental carbon, and organic carbon interact. Our results corroborate earlier work (Dasch and Cadle, 1989; Winkler, 1973, Winkler and Junge, 1972; Hameri et al., 1992) and suggest mechanisms behind field observations. Future work to quantify

surfactant coating thickness and assess the validity of extrapolating from large particles down to atmospheric particle size ranges will be important extensions of this research.

Dasch and Cadle (1989) noted that particles with high organic carbon (OC) to elemental carbon (EC) ratios were preferentially removed by precipitation. Dasch and Cadle found that carbon-containing particles removed by precipitation tended to have OC/EC ratios of 4.7 while carbon-containing ambient atmospheric particles had OC/EC ratios of 2.5. Thus particles with high OC/EC ratios are able to serve as cloud condensation and hydrometeor nuclei. This interpretation is corroborated by research showing that organic aerosol particles may make up a significant portion of CCN (Novakov and Penner, 1993). Another effect of increased hygroscopicity is a decrease in the residence time of the particle in the atmosphere. Hygroscopic particles will be removed more quickly through precipitation (Dasch and Cadle, 1989; Poeschel et al., 1981) than hydrophobic particles will be. Hence, long range transport (over distances of thousands of kilometers or periods of weeks) of carbonaceous particles will be applicable only to the hydrophobic particles which have the longer residence times in the atmosphere. Other controlling variables such as frequency of rainfall and initial particle size distribution must also be considered in residence time calculations (Ogren and Charlson, 1983).

We observed that carbon black and NaCl particles coated with surfactant sorb water gradually. This trend of smooth, continuous growth due to water uptake by mixed particles has been noted by Winkler (1973) and Winkler and Junge (1972). Their research focused on aerosol particles generated from mixtures of deliquescent salts similar in composition to atmospheric aerosol particles and showed gradual uptake of water with increasing relative humidity and gradual release of water with decreasing relative humidity. Our experiments with two component particles also demonstrate smooth gradual sorption curves.

The increase in water sorption rate observed here for carbon particles coated with organic surfactants may also have some influence on the rate of heterogeneous reactions occurring on the surface of coated carbon particles in the atmosphere. Carbon particles in the atmosphere in the presence of water can catalyze the formation of sulfates from $\text{SO}_2(\text{g})$ (Novakov et al., 1974; Smith et al., 1989). Because a surfactant coating increases the amount of water associated with carbon the rate of such reactions may increase. However, Plevan and Quinn (1966) noted that the presence of a surfactant layer decreased the adsorption of SO_2 into a liquid. The two effects due to the organic coating - increased water adsorption and decreased SO_2 adsorption - may influence the chemistry occurring on the carbon surface.

3.5 CONCLUSIONS

We have shown that an ordinarily hydrophobic carbon black particle will sorb significant amounts of water (0.2 to 0.4 the dry mass of the particle) when the particle is coated with an organic surfactant such as Tween80 or azelaic acid. This phenomenon is especially interesting in the case of surfactants such as azelaic acid, which are themselves hydrophobic. Thus, if the carbon black particles can be considered as a surrogate for elemental carbon in the atmosphere, our experiments provide evidence that if elemental carbon particles in the atmosphere are associated with certain forms of organic carbon the elemental carbon is more likely to play a role in atmospheric phenomena involving moist air (e.g., cloud and fog formation, and particle scavenging by water drops and precipitation).

The results from these experiments on carbon black particles coated with organic surfactants suggest that an organic coating increases the hygroscopicity of the ordinarily hydrophobic carbon black particles. Elemental carbon particles are often formed in combustion processes in the presence of organic vapors and are ubiquitous in the atmosphere. Because of the potential for these carbon particles to sorb both natural and anthropogenic organics, laboratory data such as presented here are important in understanding how the presence of organic compounds on the surface of these particles will affect their participation in atmospheric physics and chemistry.

3.6 TABLES AND FIGURES

Table 3.1 Comparison of experimental results with those reported in the literature for a NaCl particle.

	Observed value	Literature value	Reference
Deliquescence	75-77	75.3	Tang and Munkelwitz, 1977
Relative Humidity (%)		74-76	Cohen et al., 1987
		72-76	McMurry and Stolzenburg, 1989
		75	Winkler, 1973
Crystallization	49-54	39.5	Tang and Munkelwitz, 1977
Relative Humidity (%)		43	Cohen et al., 1987
		45	McMurry and Stolzenburg, 1989
Maximum Relative	4.0-4.2	3.75	Tang and Munkelwitz, 1977
Mass Gain (M/M_o)		4.0	Cohen et al., 1987
at Deliquescence		3.58	McMurry and Stolzenburg, 1989
Relative Humidity (%)		3.75	Winkler, 1973

Table 3.2 Effects of Tween80 on water sorption by NaCl.

Particle type	Dry particle mass M_o ($\times 10^{-11}$ kg)	Maximum relative mass gain (M/M_o) _{max} at deliq. RH%	Deliquescence Relative Humidity	Uptake time (min)
NaCl (no Tween80)	1.82-11.5	4.0-4.1	75-77%	5-10
NaCl/Tween80 5:1 - "medium" mole ratio	1.78	3.5	72-73%	20-30
NaCl/Tween80 3:1 - "low" mole ratio	7.45	1.8	70-72%	70-90

Table 3.3 Summary of experimental results comparing effects of different surfactants.

Particle type	Dry particle mass M_o ($\times 10^{-11}$ kg)	Maximum relative mass gain $(M/M_o)_{\max}$	Relative humidity at $(M/M_o)_{\max}$
Carbon Black	34.9	1.0	87%
Tween80	6.62	1.5	85%
DDS	1.02-1.2	1.0	90%
Azelaic Acid	9.7	1.0	86%
Carbon/Tween80	3.09-36.6	1.2	90%
Carbon/DDS	5.8-18	1.1-1.2	90%
Carbon/Azelaic Acid	1.64	1.4	86%

Figure 3.1 Schematic of balance chamber cross-section.

Figure 3.2 Balance system schematic (MFC = mass flow controller).

Figure 3.3a Three methods for checking data consistency: water sorption by two different particles coated in 0.01 M Tween80.

Figure 3.3b Three methods for checking data consistency: water sorption by two DDS particles injected by different methods: Particle 1 injected wet and allowed to dry; Particle 2 injected dry.

Figure 3.3c Three methods for checking data consistency: water sorption by same carbon black particle coated in 0.01 M Tween 80 for repeated relative humidity scans.

Figure 3.4 Comparison of hysteresis curves for Tween80-coated and uncoated NaCl particles. As more Tween80 is associated with the NaCl particle both deliquescence humidity and relative mass gain at the deliquescence humidity decrease.

Figure 3.5 Water uptake by an uncoated carbon black particle.

Figure 3.6 Water sorption and desorption profiles of a pure Tween80 particle and a carbon particle coated with Tween80.

Figure 3.7 Water sorption and desorption profiles of a pure DDS particle and a carbon particle coated with DDS.

Figure 3.8 Water sorption and desorption profiles of a pure azelaic acid particle and a carbon particle coated with azelaic acid.

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CHAPTER 4

ATMOSPHERIC RELEVANCE OF ELECTRODYNAMIC BALANCE RESULTS

4.1 INTRODUCTION

In the previous chapter it was shown that the electrodynamic balance is a useful tool for investigation of vapor-particle interactions similar to those which may occur in the atmosphere. The balance has many advantages. For example, single particle studies yield data without interference from other particles. Furthermore, as shown in the previous chapter, observations with a well-controlled laboratory system can illustrate possible mechanisms behind atmospheric aerosol phenomena. The balance experiments are not without disadvantages, however. The nature of the electrodynamic balance technique requires that the particle being studied is charged (on the order of 10^6 elemental charges) and is in the size range with diameters between 10 and 300 μm . These charge and size requirements mean that the particle under study can be quite different from particles typically found in the atmosphere. In this chapter it is shown that, despite the differences in particle characteristics, the results from electrodynamic balance studies are still atmospherically relevant.

4.2 EFFECT OF CHARGE ON BALANCE RESULTS

In the atmosphere, particle charge may play a role in cloud and rainfall dynamics. It has been suggested that the particle charge enhances the collision efficiency of cloud droplets and thus influences the evolution of precipitation-sized particles (e.g., Ochs and Czys, 1987). Additionally, it has been shown that electrical charge can influence the growth and shape of ice crystals in the atmosphere (e.g., Evans, 1973). In the particle balance lab, the question often arises as to whether the sign and or amount of the charge on a particle - which is necessary for particle suspension in the balance - affects the phenomena being studied. For example, in salt deliquescence studies where the growth of a salt crystal as a function of relative humidity is investigated, it is possible that the charge on the particle could influence the rate and/or amount of water uptake or even the deliquescent relative humidity. In this section, theoretical and experimental evidence is presented which suggests that neither the sign nor the amount of charge influences the water uptake of salt particles suspended in the electrodynamic balance.

Many researchers have conducted condensation/evaporation experiments in electrodynamic chambers (e.g., Davis et al., 1978; Zhang and Davis, 1987; Sageev and Seinfeld, 1984). Others have studied charged particle fission as highly charged, evaporating droplets approach the Rayleigh charge limit (e.g., Taflin et al., 1989; Doyle et al., 1964). These studies assumed that the effects of charge on the rates of evaporation and condensation were negligible. This assumption is supported by a theoretical analysis by Law and Bowen (1975) on the influence that the charge on a droplet has on evaporation. They considered a force balance on a single charged droplet in a non-convective environment and

showed that for single pure water droplets charged to the Raleigh limit, that evaporation rate is a constant, independent of drop radius, for droplets of radius greater than $0.1\ \mu\text{m}$. They found, however, that for uncharged water droplets less than $0.1\ \mu\text{m}$ radius the evaporation rate increases as the radius decreases. Law and Bowen noted that their analysis depends on the droplet's surface energy. Because surface energy changes with droplet composition different results would be found for different types of particles and droplets. In a later paper Law (1989) experimentally investigated the effects of charge on evaporation rate by measuring the amount of mass evaporated from charged and uncharged droplets hanging from a micropipette tip. Droplet charge level did not appear to have a significant effect on droplet evaporation rates.

4.2.1 Theoretical calculations

Law and Bowen (1975) investigated how the presence of a charge on the droplet would change the surface energy of the droplet and thus potentially influence mass transfer from the droplet surface. The approach used here is to investigate how droplet charge creates an electric field around the droplet which could potentially influence water vapor mass transfer toward the droplet surface. Table 4.1 lists the parameters and constants used in these calculations. In section 4.2.3 experimental results from the electrodynamic balance for this same system are presented. Water vapor molecules are not ions which could clearly be affected by a particle charge, but they do have a dipole moment, and the charge on the droplet may affect the orientation of the vapor molecules with respect to the droplet. If the charge on the droplet is able to affect the orientation of the vapor molecules it could very well change the flux of the molecules to the surface and thus alter the uptake rate or deliquescence relative humidity. It should be noted that the assumption in this study is that the balance fields themselves are not affecting the droplet/vapor system. In other words, it is assumed that the only electrical effects are those caused by the charge on the suspended saline droplet. This is a reasonable assumption, because the electric field generated by the ring electrode has a null point (i.e., there is no field) in the center of the balance chamber in which the particle is suspended. The vertical electric field produced by the endcap electrodes would have an equal but opposite effect on each side of the suspended particle and thus have a no net effect on particle growth. Just for reference, the vertical dc field in the balance is on the order of $1,000\ \text{V/m}$, while in the atmosphere the fair weather field is $100\ \text{V/m}$ and the thunderstorm field is $10,000\ \text{V/m}$ (Rogers and Yau, 1989).

The general assumption amongst researchers using the electrodynamic balance is that the charge on the suspended particle/droplet does not affect the phenomenon being studied. In these calculations, then, a worst case scenario approach is used and the effects of droplet charge are studied where those effects would be strongest, i.e., very close to the droplet surface. Both the energetics and molar fluxes of the system are investigated in order to see the influence of charge. First, the thermal energy of the water

vapor molecules is compared with their rotational energy to determine whether the droplet charge is able to align the dipolar water vapor molecules. Then, the electrical and diffusive fluxes of water vapor molecules to the droplet surface are compared. As is shown in what follows, even with "preferential treatment", the effect of droplet charge on molecular orientation and flux is negligible compared to other (diffusive, thermodynamical) effects.

4.2.2 Effect of charge on motion of water vapor molecules

In this section, the thermal energy of the water vapor molecules is compared to their potential (or electric) rotational energy in the electric field created by the presence of the charged droplet. The thermal energy is the energy due to the vapor molecules' motion. In the absence of an external field (e.g., the electric field generated by the charged droplet) collisions and thermal motion would cause the water vapor molecules to be randomly aligned in space. The rotational potential energy can be defined as the energy required to align the randomly organized water vapor molecules in the direction of their dipoles. It can be hypothesized that if the thermal energy of the water vapor molecules is much greater than their rotational potential energy then the vapor molecules are not likely to be affected by the charge on the suspended droplet. If there is a preferred alignment of the dipoles (i.e., the rotational potential and thermal energies are comparable) then there will be a net acceleration of the vapor molecule toward the droplet, due to the electric field of the charged droplet. Thermal energy is approximately (Conway, 1981):

$$E_{\text{thermal}} = kT \quad 4.1$$

where k is Boltzmann's constant = 1.382×10^{-16} erg/K, and T is temperature = 298 K. We find that E_{thermal} is approximately 4.12×10^{-14} erg = 4.12×10^{-21} joules.

The rotational potential energy, E_{pot} , is calculated by integrating:

$$dE_{\text{pot}} = F_{\text{elec}} dr \quad 4.2$$

between $r = r_p$ at the surface of the saline drop, to $r = \text{infinity}$. F_{elec} is the force exerted on a dipole (the water vapor molecule) by a charged particle and is given by (Purcell, 1985):

$$F_{\text{elec}} = 2pQ/r^3 \quad 4.3$$

Here p is the dipole moment of a water molecule = 1.84×10^{-18} esu-cm, Q is the charge on the saline droplet in esu, r is the distance from the center of the droplet in cm. The integration gives:

$$E_{\text{pot}} = -pQ/r_p^2 \quad 4.4$$

Plotting E_{pot} as a function of r_p and particle charge compared to E_{thermal} at $T = 298 \text{ K}$ as shown in Figure 4.1, we see that E_{thermal} is larger than E_{pot} by at least one order of magnitude for r_p in the size and charge range of importance in the balance (i.e., $r_p > 6 \mu\text{m}$ and $q < 9 \times 10^{-4} \text{ esu}$). Thus it can be concluded that for typical conditions in the balance, the charge on the particle does not affect the motion/alignment of the water vapor molecules surrounding the charged particle. For charge levels typically seen in the balance, E_{pot} only becomes significant for particles with r_p smaller than approximately $2 \mu\text{m}$. In the atmosphere, particles rarely reach the level of charge observed on balance particles (except perhaps in thunderstorm clouds). The charge on atmospheric particles tends to be represented by a Boltzmann distribution which means that for the smaller particles ($dp < 1.0 \mu\text{m}$) there are generally less than 10 fundamental charges. For a $0.1 \mu\text{m}$ particle, this corresponds to a potential rotational energy on the order of $2 \times 10^{-16} \text{ dynes-cm}$, several orders of magnitude smaller than the thermal energy. Thus, for atmospheric particles, particle charge is unlikely to influence particle growth

Another approach for determining the effects of the charged droplet on the motion of the surrounding water molecules is to compare the fluxes of water molecules to the particle surface due to diffusive forces and due to electrical forces. To do this the flux is separated into components of diffusive and electrical flux:

$$j_i = j_{\text{diff}} + j_{\text{elec}} \quad 4.5$$

This superpositioning of fluxes is the approach used to determine ion fluxes in solution in the Nernst-Planck ion flux equation (Cussler, 1988). Now the appropriate flux equations for j_{diff} and j_{elec} for water vapor molecules in air in the presence of the charged particle must be determined. The concentration gradient-driven diffusion flux of a vapor molecule i to sphere of r_p is given by (Seinfeld, 1986):

$$j_{\text{diff}} = 4\pi r_p D (C_{i,\text{inf}} - C_{i,\text{surf}}) \quad 4.6$$

where r_p is the radius of the droplet, D is the diffusion coefficient of species i (here water vapor) in air, $C_{i,\text{inf}}$ is the concentration of species i at infinity (assumed here to be $5.79 \times 10^{23} \text{ molec water vapor/m}^3$ which is equivalent to 75% relative humidity at STP), and $C_{i,\text{surf}}$ is the concentration of species i at the droplet surface (assumed here to be 0, which is equivalent to 0% relative humidity).

The above flux equation (4.6) is applicable when $2r_p \gg l$, the mean free path of the vapor molecule. For the conditions considered here, the mean free path of the water vapor molecule is about $0.05 \mu\text{m}$ which is much less than particle diameters ($1\text{--}100 \mu\text{m}$) in which we are interested. Thus equation 4.6 is considered applicable.

For the electric flux, a simple model is used (developed from a mass balance equation) for flux of species i :

$$j_{elec} = C_i A V_d \quad 4.7$$

where C_i is the concentration of species i (a function of r), A is the area of the surface towards which species i is moving, and V_d is the velocity with which species i moves toward the surface.

C_i and A can be calculated for the electrodynamic balance conditions but V_d is still needed. Hinds (1982) derives an equation for the terminal velocity of a charged particle in an electric field by setting the electrostatic force equal to the force due to Stokes drag.

$$F_e = 6\pi\mu r_i V/C_c \quad 4.8$$

where V is the Stokes velocity, μ is the viscosity of air, r_i is the radius of species i , and C_c is the Cunningham slip correction factor (C_c is 263 for a water molecule in air).

A similar approach is used here, but in place of Hinds' force on a charged particle in an electric field ($F_e = qQ/r^2$) the force on a dipole in an electric field ($F_e = 2pQ/r^3$) is used where p is the dipole moment, Q is the charge on the droplet, and r is the distance of the dipole from the center of the droplet.

The velocity of a water vapor molecule in air in the presence of the electric field created by the charged droplet is then:

$$V_d = (C_c/6\pi\mu r_i) (2pQ/r^3) \quad 4.9$$

($C_c/6\pi\mu r_i$ is often referred to as the particle mobility, "B" (Hinds, 1982) and particle velocity can be determined from the relation: velocity = force*mobility). Equation 4.9 yields a water molecule velocity of $1.2e-3$ m/s using the values listed in Table 4.1. While the determination of ion flux in aqueous solutions uses the above method (equation 4.9) to calculate ion velocity, it is admittedly questionable whether use of the Cunningham correction factor, C_c , is appropriate for a single water molecule due to the small size ($r = 3.2e-10$ m) of the molecule. For an ion in solution, Bockris and Reddy (1970) suggest that the Stokes law may yield velocities off by greater than 50%. However, other methods for calculating ion and dipole mobilities in electric fields (e.g., Liu and Yeh, 1968; Wahlin, 1994) yield even smaller velocities and thus smaller fluxes than calculated using the Stokes drag force.

Figure 4.2 compares j_{diff} and j_{elec} as a function of r_p . The flux due to diffusion is at least two orders of

magnitude larger than the flux due to electrical forces for typical particles observed in our balance, and thus it can be assumed that the charge on the droplet does not affect the flux of water vapor molecules to the droplet. Extrapolating Figure 4.2 for smaller particles ($d_p < 2.0 \mu\text{m}$) suggests that electrical and diffusive fluxes become comparable if the droplet charge is similar to that required for balance particles. Atmospheric particles (not in clouds) tend to be in an equilibrium charge state described by the Boltzmann distribution. The majority of these particles tend to have single digit number of charges on them ($< 5e-9$ esu) and thus the resultant flux due to the particle's electrical charge for a $1 \mu\text{m}$ particle would be on the order of $1e-14$ molec/sec which is four orders of magnitude less than the diffusive flux for the same particle. These typical atmospheric particles would have even smaller electrical flux as they are less charged. From these calculations it also can be concluded that the growth of typical atmospheric particles will not be influenced by their charge.

4.2.3 Experimental results

Table 4.2 gives deliquescence relative humidities and relative mass gains for uncharged NaCl particles (studies other than electrodynamic balance) and charged NaCl particles (electrodynamic balance experiments). Table 4.2 suggests that charge on a particle may result in higher observed relative mass gains although other experimental factors (e.g. using convective systems) may also be the reason for the higher relative mass gains (around 4.0) observed by Cohen et al. (1987) and Andrews and Larson (1993). Thus, further experiments were done to determine if changes in deliquescence humidity and/or maximum relative mass uptake could be attributed to the amount of charge on the suspended particle. Differences in deliquescence time were also studied.

In the experimental portion of this study, observations were made on a number of individual NaCl particles in the electrodynamic balance. The particles studied varied in size, sign of charge and in the amount of charge. Table 4.3 lists values for charge and mass of the particles used in this portion of the experimental work. Table 4.3 shows that for the particles studied there was an order of magnitude variation in the particles' masses and their charge to mass ratio, and a two orders of magnitude variation in the particles' charges.

Figure 4.3 is a plot of hysteresis curves for the positively and negatively charged particles listed in Table 4.3 developed by observing the individual particle response to changes in relative humidity. The particles appear to follow the same hysteresis path despite differences in particle size, and amount and sign of particle charge. This result is also in agreement with the calculations in the previous sections which suggested that effects of charge on mass uptake and deliquescence relative humidity would be negligible for balance size ($10\text{-}100 \mu\text{m}$) particles.

Figure 4.4 is a plot of particle radius squared versus time for several positive and negative particles as they undergo deliquescence. (One would expect the relationship between time and radius squared to be linear if the system is dilute and the water vapor concentration is constant far from the particle and zero at the particle surface (Seinfeld, 1986).) The fact that the slopes of the lines in Figure 4.4 (see Table 4.3) are within a factor of two despite the large differences in particle charge and size suggests that the particle growth rates are not affected by the charge on the particle. This is further supported by there being little or no correlation between the slope of these lines and particle charge or charge-to-mass ratio. The higher M/M_0 values reported for the charged particles in Table 4.2 are thus probably due to other experimental differences. For example, in a forced convection system with continuous flow past the droplet, the average vapor concentration seen by the particle might be higher than in a free convection system where the vapor concentration is controlled solely by diffusion to the particle. Comparison of Nusselt numbers (an indication of mass transfer) for both forced and free convection systems shows that mass transfer to a droplet is more efficient for the forced convection system. Another possible mechanism for increases in M/M_0 is that there could be increased vapor deposition on the upstream side of the particle not balanced by mass loss on the downstream side, although Fukuta (1992) notes that in the Stokes' flow regime the rate of growth on the front face of the droplet is equal to the loss on the back side of the droplet and thus growth is the same as for a droplet with no velocity relative to its surroundings.

4.2.4 Application to atmospheric systems

The electrodynamic balance research takes place in controlled laboratory conditions. It is interesting to compare some of these conditions to those observed in the atmosphere. Figure 4.5 is a compilation of data from Takahashi (1973) (taken from Pruppacher and Klett, 1980) showing charges measured on atmospheric droplets (rain and cloud drops) as a function of droplet size. Typical experimental data points from the electrodynamic balance have been added to the plot. The electrodynamic balance particles are more highly charged than typical atmospheric droplets in the same size range. Because it was shown above that particle charge did not influence particle growth in the balance it is to be expected that the effect of electric charge on atmospheric droplet growth will also be negligible.

4.3 EFFECT OF PARTICLE SIZE

It is important to understand the role particle size plays in laboratory and field aerosol measurements. Size is an important parameter because it can influence a particle's transport properties, residence time, light scattering properties and ability to act as a cloud or ice nuclei. Typical balance experiments are done with particles with diameters in the size range from 10-300 μm . However, particles of interest in the atmosphere range from 0.01 μm for CCN to 100s of μm for raindrops (Rogers and Yau, 1989). While the electrodynamic balance can easily be used to investigate the larger end of this size range,

often times information is desired about particles smaller than $2\text{ }\mu\text{m}$ or in the submicrometer size range. Here electrodynamic balance experiments are compared with another particle measurement technique to determine whether balance results can be reasonably applied to atmospherically relevant particle/vapor systems.

4.3.1 Comparison of electrodynamic balance and tandem differential mobility analyzer techniques
The tandem differential mobility analyzer (TDMA) (for example, McMurry and Stolzenburg, 1989) and the electrodynamic balance are common instruments for studying aerosol phenomena. Despite similar research applications, the TDMA and electrodynamic balance operate under quite different experimental conditions. These differences are compared in Table 4.4 and some are discussed in further detail below.

The TDMA measures changes in particle diameter following some sort of conditioning (i.e., exposure to relative humidity) based on changes in particle mobility. Particle mobility measurements depend upon knowing the charge on the particle, and often the particles are passed through a neutralizer prior to entering the TDMA in order to attain particles which are mostly neutral or singly charged. Unlike the electrodynamic balance in which a single particle's response to conditioning is observed, in the TDMA a continuous stream of particles is generated and passed through the system. In order to obtain statistically significant diameter measurements a population of the droplets must be observed. Additionally, because the particles studied in the TDMA move along with the gas stream, their residence time in the system is short, potentially shorter than the time required for equilibrium with the conditioning gas stream. One of the most noteworthy differences between the two devices is the particle size range which can be studied in them. The TDMA is used to observe particles in the size range $0.01 - 1.0\text{ }\mu\text{m}$, the size range of interest for CCN investigations, while particles studied in the electrodynamic balance are typically between 10 and $300\text{ }\mu\text{m}$, on the order of cloud or raindrops. Below we compare experimental results from these two devices and discuss the atmospheric implications.

4.3.2 Comparison of experimental results

In Figure 4.6 (Andrews et al., 1993) experimental results from an electrodynamic balance and a TDMA (Rood et al., 1993) for a pure NaCl particle hysteresis cycle are compared. Both results agree well with the experimentally derived model curve based on results from Tang and Munkelwitz (1977) and for relative humidity greater than 75% and results from Cohen et al. (1987) for the metastable particles at relative humidities less than 75%. The agreement between the two experiments is excellent, considering that the particles were approximately two orders of magnitude different in diameter. Differences in the results could be due to several factors. The difference could be due to the non-spherical shape of the particles studied. The shapes of particles in the electrodynamic balance can be highly irregular, although a spherical particle is assumed in data analysis. The TDMA particles are

cubical due to the salt crystalline structure although an equivalent spherical diameter is assumed for the measurement technique. Furthermore, converting from the particle mass measured by the electrodynamic balance to particle diameter for comparison with TDMA results could induce error as the density is not exactly known for supersaturated salt droplets. Other differences could be attributed to experimental parameters listed in Table 4.4 such as forced versus free convective gas flow and particle population and residence time in the conditioning flow.

Figures 4.7 and 4.8 are typical experimentally measured hysteresis curves from the electrodynamic balance and TDMA (Rood et al., 1993) for NaCl particles coated with unquantified amounts of octanoic acid (a hydrophobic organic). Comparing these two figures it can be seen that the TDMA and electrodynamic balance particle measurement techniques give different results. In the case of the electrodynamic balance measurements, the presence of the organic did not appear to affect the deliquescence humidity or the total amount of water taken up by the particle during deliquescence (although the deliquescence rate is slower when organic is present (Andrews and Larson, 1993; Wagner, 1995)). However, the presence of the organic does appear to lower the particle crystallization humidity. In the case of the TDMA results it is difficult to determine whether the presence of the organic influences the particles' deliquescence or crystallization humidity. The organic coating does appear to lower the total amount of water taken up by the particle. The question is whether the differences between these two sets of experiments are due to differences in particle size or to differences in the measurement techniques.

Fletcher (1958) made theoretical calculations studying the size dependence of heterogeneous nucleation/condensation on particles, based on particle size and hygroscopicity. His calculations suggest that the influence of particle size increases with particle hydrophobicity (See Figure 4.9). Figure 4.9 shows that for greater hydrophobicity, indicated by smaller values of m ($m = \cos \theta$ and θ is the contact angle), the slope of saturation ratio versus particle radius is steeper than for less hydrophobic particles. Based on this result, it would be expected that the coated TDMA particles would require higher humidities to grow than would the coated electrodynamic balance particles (assuming that the coatings were the same, e.g., thickness, coverage, etc.).

Additionally, based on Fletcher's calculations, hydrophobic particles would require higher humidities to experience condensational growth than a hygroscopic particle. This is consistent with the TDMA observations (e.g., Figure 4.8) that at a given humidity the organic-coated (i.e., hydrophobic) particles appear to have less water uptake than the uncoated (i.e., hydrophilic) particles, however, such an effect is not noticed for the electrodynamic balance studies on coated particles (e.g., Figure 4.7). This suggests that the observed differences in the two sets of experiments is due to the differences in

experimental parameters. The three parameters most likely to play a role would be the amount of coating and coating method, the residence time in the humidity conditioner, and the number of particles competing for coating/water. In these experiments the amount of coating is not quantified, although complete and even coverage is assumed. The TDMA particles, after exposure to the coating vapor, have much less residence time (order of seconds) in the humidity conditioner where they may uptake water, while the coated particle in the electrodynamic balance is exposed to a humidified air stream (order of minutes) until it has reached its equilibrium mass. In both the TDMA and electrodynamic balance experiments the coated particles take up water at relative humidities close to the deliquescence humidity for pure particles, suggesting that the particles in both cases have irregularly coated surfaces with some hygrophilic material exposed.

4.3.3 Application to atmospheric systems

Particles in the atmosphere range from 0.01 μm for CCN to 100s of micrometers for raindrops (Rogers and Yau, 1989). The work of Orr et al. (1958) showed size effects for particle growth rates for particles in the size range 0.01-0.1 μm . They attributed the size effects to surface tension differences for the different sized particles. Basically, this is the same approach as the Kelvin effect which looks at the balance between curvature and surface tension as a function of size. The experiments of Orr et al. (1958) showed that small salt particles (spherical equivalent $d_p < 0.1 \mu\text{m}$) deliquesced and grew at lower humidity than larger salt particles which deliquesced at the bulk deliquescence relative humidity. Neither the TDMA or electrodynamic balance particle experiments discussed here demonstrate a particle size dependence for deliquescence relative humidity or water uptake amount. However, the particles considered here still had diameters larger than 0.1 μm . From this, we can conclude that for hygroscopic particles with $d_p > 0.1 \mu\text{m}$ the TDMA and the electrodynamic balance will yield equally useful and atmospherically relevant results.

A comparison of TDMA and electrodynamic balance experimental results for hygroscopic particles coated with a hydrophobic organic does show mass uptake differences, although the deliquescence relative humidity was not noticeably affected by the presence of a coating for either measurement technique. Based on theoretical work (e.g., Fletcher, 1958; Warner and Warne, 1970) for hydrophobic particles, one would expect coated particles to behave differently than uncoated, hygrophilic particles. In order to extend the TDMA and electrodynamic balance experimental results for coated particles to atmospheric systems, further work to quantify the experimental coating techniques is necessary.

4.4 CONCLUSIONS

The electrodynamic balance is a good technique for studying aerosol systems of interest in the atmosphere as well as for a variety of other applications. It has been shown that particle charge does

not influence experimental results in electrodynamic balance studies. Thus, the fact that the particles are charged does not affect the results' applicability to atmospheric systems. Comparison of TDMA and electrodynamic balance results show that for particles greater than 0.5 μm diameter, the size of the laboratory particle is not likely an issue for atmospheric relevance. Similar experimental results were obtained for particles in both systems despite the two order of magnitude difference in particle size.

We will mention one caveat, however. For multiparticle systems both charge and size may play a role in particle-particle interactions such as coagulation and coalescence (Ochs and Czys, 1989).

Furthermore, depending on the particle concentration in multi-particle systems, particle-vapor interactions may also be influenced by size and/or charge. For example, it has been shown, in Chapter 2, that gas-to-particle conversion can be inhibited if there are enough existing particles with enough associated surface area to preferentially collect and deplete vapor. In the next chapter competitive growth is investigated using a prototype device (the RITDC) to simultaneously monitor growth of particles of several compositions.

4.5 TABLES AND FIGURES

Table 4.1 Values of constants and parameters used in calculations.

	Values of constants	Reference
Dipole moment of water vapor	1.84×10^{-18} esu-cm	(Purcell, 1985)
Diffusion of water vapor in air	2.6×10^{-5} m ² /s	(Cussler, 1988)
Boltzmann constant	1.38×10^{-16} erg/K	(Purcell, 1985)
Temperature	298 K	
Pressure	1 atm	
Viscosity of air	1.85×10^{-5} kg/m-s	(Wark & Warner, 1981)
Radius of water molecule	3.16×10^{-10} m	(Seinfeld, 1986)

Particle parameters

radius (Rp)	15 μ m 1.5×10^{-5} m
density	1.281 g/cm ³ (of aqueous 5.5 M NaCl droplet)
charge	4.8×10^{-5} esu, 10^5 fundamental charges, 4.4×10^{-18} moles charge = moles electrons
molarity	5.5 moles NaCl/liter water 4.4×10^{-10} moles NaCl/droplet 4.4×10^{-9} moles water/droplet
water vapor	75% relative humidity 23,479 ppm 5.79×10^{23} molecules/m ³

Table 4.2 Some literature values for NaCl hysteresis parameters.

Reference	Deliq. RH%	Rel. Mass (M/Mo)	Rel. Size (D/Do)	Number of charges
McMurry and Stolzenburg, 1989	72-76	3.58	1.88	0-1
Winkler, 1973	75	3.75	1.96	??
Tang and Munkelwitz, 1977	75.3	3.75	1.9	10^5
Cohen et al., 1987	74-76	4.0	1.96	10^5
Andrews and Larson, 1993	75-77	4.0-4.1	1.96-2.0	10^5

Table 4.3 Approximate charge and mass values for experimental runs.

Particle ID	particle mass (kg)	particle charge (C)	charge/mass ratio (C/kg)	particle radius (μm)	slope in Figure 4.4
pos1	8.1×10^{-12}	4.9×10^{-15}	6.1×10^{-4}	9.6	$38 \mu\text{m}^2/\text{min}$
pos2	8.1×10^{-11}	1.7×10^{-13}	2.1×10^{-3}	21.0	83
neg1	2.6×10^{-11}	4.7×10^{-14}	1.8×10^{-3}	14.2	63
neg2	5.5×10^{-11}	3.0×10^{-13}	5.5×10^{-3}	18.2	72

Table 4.4 Comparison of electrodynamic balance and TDMA characteristics.

	electrodynamic balance	TDMA
Particles	single highly charged (10^6 esu) $10 < dp < 300 \mu\text{m}$	Population of particles Boltzmann charge distribution (~ 10 esu) $0.01 < dp < 1.0 \mu\text{m}$
Gas Flow	variable ($\sim$ particle settling velocity)	sample air - 0.3 lpm sheath air - 10 lpm
Residence time	long term (hours - days)	~ 2 seconds
Measurement	particle mass proportional to voltage	particle equivalent diameter function of electrical mobility

Figure 4.1 Thermal and potential energy as a function of particle size for a range of particle charge.

Figure 4.2 Comparison of charge and diffusion induced flux of molecules to particle as a function of particle size and charge.

Figure 4.3 Comparison of hysteresis curves for positively and negatively charged NaCl particles.

Figure 4.4 Comparison of growth rates at deliquescence for positively and negatively charged NaCl particles.

Figure 4.5 Comparison of electric charge on cloud and raindrops to charge on particles studied in the electrodynamic balance (with changes from Takahashi (1973)).

Figure 4.6 Comparison of TDMA and electrodynamic balance hysteresis curves for NaCl compared with modelled hysteresis curve (Tang, 1977; Cohen et al., 1987).

Figure 4.7 Comparison of hysteresis curves for pure and octanoic acid-coated NaCl particle observed in the electrodynamic balance. Note the y-axis is relative mass, M/M_0 .

Figure 4.8 Comparison of hysteresis curves for pure and octanoic acid-coated NaCl particle observed in the tandem differential mobility analyzer (TDMA). Note the y-axis is relative diameter, D/D_0 .

Figure 4.9 Equilibrium saturation ratio as a function of particle size for various particle hygroscopicities.

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CHAPTER 5

A PROTOTYPE DEVICE FOR MULTI-PARTICLE GROWTH EXPERIMENTS

5.1 INTRODUCTION

In this chapter a method is proposed for studying competition for water vapor by an assembly of particles of differing composition. Preliminary data for characterizing this prototype device are also presented. Currently, there exists no experimental device for simultaneously monitoring a finite number of particles of known composition in a changing environment. As the modelling study in Chapter 2 showed, the number of particles present in a volume of air strongly influences the growth characteristics of the particle population. By being able to directly compare response of particles of different compositions to changing environmental conditions we may infer the types of particles that may be activated in a cloud, an industrial application or other particle/vapor interaction scenarios. The prototype device is called the Refractive Index Thermal Diffusion Chamber or RITDC (pronounced ritzy).

The RITDC is an apparatus which combines aspects of two extant devices - the refractometer which measures refractive index and the thermal diffusion chamber (TDC) which is used to observe particle growth in controlled saturation ratio conditions. In this chapter the theory of each of these devices relevant to the RITDC is developed and experiments to characterize the prototype RITDC are performed. Experiments include tests of environmental control in the RITDC chamber and characterization of the RITDC optical system.

It is well understood that in a cloud containing supercooled water droplets and ice crystals, the ice crystals will preferentially grow first by vapor diffusion and then at the expense of the water droplets, due to the lower equilibrium water vapor pressure over ice. In other words, the cloud droplets evaporate and the lost water vapor goes diffuses to the growing ice crystals. This is known as the Wegener-Bergeron-Findeisen precipitation growth mechanism. In a warm cloud it has been noted that once the activation stage in a cloud is past (after the maximum supersaturation is achieved) the activated droplets compete for the remaining vapor while the unactivated drops remain unchanged (Fukuta, 1992).

This idea of competition for water vapor can be extended to other particle/vapor systems. For example, the results of the various studies investigating the influence of organic coatings on particle growth characteristics due to vapor deposition suggest important implications in a population of particles competing for the same vapor. A modelling study by Podzimek and Saad (1975) also demonstrated the effect of competitive growth on a cloud droplet size distribution. They used a one dimensional cloud model to investigate the influence that the presence or absence of an organic coating on condensation

nuclei had on the growth and stability of cloud or fog droplets. In the uncoated case, the particles in the eleven modelled size ranges grew; but, when the eleven section array consisted of organic-coated condensation nuclei, the presence of an organic coating enabled the smaller nuclei to grow while the larger nuclei did not. The smaller nuclei were able to overcome the protective capability of their organic layer more quickly and grow, thus lowering the saturation ratio and preventing the growth of larger particles.

For the NaCl/organic/water system described in Chapter 3, several of the characteristic effects of organic layers on liquid drops were observed which have also been noted in other studies (Wagner, 1995; Otani and Wang, 1984; Snead and Zung, 1968; Rubel and Gentry, 1984). Specifically, in Chapter 3, we saw that the rate of water scavenging by an organic-coated NaCl particle was slower than that for an uncoated particle. This lowered water uptake rate was observed for both octanoic acid- and Tween80- coated particles (Andrews et al., 1993; Andrews and Larson, 1993). Figure 5.1 (Andrews et al., 1993) shows relative mass as a function of time for pure NaCl and for NaCl particles coated with octanoic acid exposed to a relative humidity of approximately 75%. The increasing relative mass is due to water uptake by the particle. The difference between the two curves indicates that the organic coating is affecting the surface kinetics of the deliquescent NaCl particle and influencing the particle's growth rate. Otani and Wang (1984) observed similar decreases in water sorption rates for coated NaCl droplets. One explanation for these observations is that the hydrophobic organic coating has a low accommodation coefficient for water vapor and thus slows the equilibration of the NaCl particle with its humid environment.

It has been suggested that particles of different composition (e.g., coated versus uncoated) existing in the same air parcel will compete for the finite supply of water vapor available to them (Gill et al., 1983). Having shown that a deliquescent salt particle coated with an organic surfactant sorbs water slower than does an uncoated deliquescent salt particle, the question arises: if the coated and uncoated particles were in the same air parcel, will the uncoated particle sorb all the water vapor while the coated particle stays dry or unactivated? This competition for vapor among particles is difficult to model as the effects of particle composition on competition for vapor have not been well quantified.

One approach to understanding the influence of composition on growth is to incorporate fundamental parameters which are affected by composition (e.g., surface tension or hygroscopicity) into modelling studies. For example, lowered droplet surface tensions due to the presence of dissolved organics have been observed in both field and laboratory work (e.g., Capel et al., 1990; Valsaraj, 1988). Modelling results have shown that by including the influence of surface tension when modelling the evolution of a cloud droplet population changes the shape of the modelled cloud droplet size distribution (Srivastava,

1991). Since surface tension is a function of composition, it can be inferred that composition of the droplets may also be a factor in the evolution of a size distribution and may determine particle activation and subsequent growth. Shulman et al. (1994) made solubility measurements and plotted Kohler curves for aqueous ammonium sulfate droplets containing various dicarboxylic acids. They showed that, if the organic lowered the surface tension of the droplet, the equilibrium growth parameters of the droplet changed. Specifically, the critical radius increased with decreasing surface tension, while the critical supersaturation decreased. Thus, using a combined modelling and fundamental measurements approach much, can be learned. However, experimental measurements are also necessary in order to validate modelled results, and the RITDC provides a new method for measuring compositional effects on particle growth.

The RITDC has been developed to monitor competition for water vapor, although in its current form, only qualitative results can be obtained from the device. Results from this apparatus investigating particle competition for water vapor can be compared, qualitatively, with results from other particle growth studies (e.g., single particle EDB experiments described in Chapter 3 and the TDMA work discussed in Chapter 4) and incorporated into modelling studies. Further refinements to the prototype device are suggested which would enable quantitative results to be obtained as well.

5.2 METHODS

In this research the RITDC prototype device has been developed to observe competition for water vapor among particles of differing composition. This modified thermal diffusion chamber (TDC) differs from the traditional TDC in two ways. First, it is used for sub-saturated experiments, i.e., relative humidities of less than 100% are generated at the chamber midpoint. Second, rather than observing a random population of particles, only two or three particles at a time are studied and it is assumed that the composition of each particle is known *a priori*. The particles being studied are suspended on an optical waveguide support at the chamber midpoint instead of freely suspended in the chamber volume. Water sorption by uncoated and coated particles may be observed in this modified thermal diffusion chamber. Particles of the same core composition can be exposed to the same environment at the same time, hence, differences in water sorption would be due solely to the existence and/or composition of a coating. The number of compositions of particles that can be studied in the RITDC is limited only by the number of waveguides and light detectors in the system.

The instrument is based on the principal that the particle's index of refraction changes as the particle responds to changes in the chamber humidity. This causes changes in light transmission through the optical waveguide support from which particle phase and particle growth rates are determined using optical waveguide theory. This is discussed in detail in the optical waveguide theory section (Section

5.2.2). The preliminary experiments described in this chapter test the hypothesis that, in an environment with a limited water vapor supply, particles compete to sorb vapor and their success depends on their hygroscopicity.

There are several advantages of using the modified thermal diffusion chamber for these types of experiments. First, one can observe the behavior of several particles or materials exposed to the same environment simultaneously. This set-up is also safe - it requires no high voltage power supplies or other potentially hazardous pieces of equipment. Additionally, the experiments (in their present incarnation) are not time intensive due to the fact that once the experiment is started, a computer or chart recorder takes the data. The disadvantages of the current system, unfortunately, relate to its applicability to atmospheric phenomena. Atmospheric particles are not supported by glass rods; nor are the particles several millimeters in diameter!

5.2.1 Thermal diffusion chamber theory

Before discussing the optical waveguide theory used to monitor particle response to changes in relative humidity in the prototype device, thermal diffusion chamber (TDC) theory and the modifications to the traditional TDC design are described. Research on cloud processes and CCN activation often requires the production of supersaturated vapor. For example, in order to be able to grow and sustain an ice crystal, saturations greater than or equal to ice saturation must be achieved. One method for producing ice and water supersaturations is the TDC. The traditional TDC (see Figure 5.2) consists of two horizontal flat plates coated with ice or wet filter paper to supply water vapor. The plates are held at different temperatures and the temperature differential between the plates creates both a linear water vapor pressure gradient (equation 5.1a) and a linear temperature gradient (equation 5.1b) between the plates (Rogers and Yau, 1989):

$$p(z) = p_2 + \frac{p_1 - p_2}{h} z \quad (a) \quad T(z) = T_2 + \frac{T_1 - T_2}{h} z \quad (b) \quad 5.1$$

where $p(z)$ is the vapor pressure in the chamber as a function of height z ($z = 0$ at the bottom plate); p_2 and p_1 are the equilibrium vapor pressures at the plates and h is the separation between the plates.

Likewise for equation 5.1b, $T(z)$ is the temperature in the chamber as a function of height and T_1 and T_2 are the temperatures of the two plates. Combining equations 5.1a and b and defining saturation as $S = p/p_{\text{equilib}}(T)$ where p is the actual vapor pressure and p_{equilib} is the equilibrium vapor pressure (a function of T) we can arrive at an expression for the saturation ratio in the chamber (Saxena et al., 1970):

$$S = \left(\frac{T(z) - T_2}{T_1 - T_2} \right) \frac{p_1 - p_2}{p_{\text{equilib}}} + \frac{p_2}{p_{\text{equilib}}} \quad 5.2$$

The saturation ratio in the center of the chamber ($z = h/2$) becomes:

$$S_{\text{mid}} = \frac{P_{\text{mid}}}{P_{\text{equilib}}(T_{\text{mid}})} = \frac{p_1 + p_2}{2P_{\text{equilib}}(T_{\text{mid}})} \quad 5.3$$

Because of the exponential dependence on of the Clausius-Clapeyron equation on temperature (Rogers and Yau, 1989):

$$P_{\text{equilib}}(T_{\text{mid}}) = p^{\circ}(T_o) \exp \left[\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_{\text{mid}}} - \frac{1}{T_o} \right) \right] \quad 5.4$$

(where p° is the saturation vapor pressure of water at temperature T_o , ΔH_{vap} is the latent heat of vaporization and R is the ideal gas constant) S_{mid} , the ratio of the actual vapor pressure in the middle of the chamber, $(p_1 + p_2)/2$, to that predicted by the Clausius-Clapeyron equation, p_{equilib} , is greater than one and a supersaturated region is created in the center of the diffusion chamber. Figure 5.3a is a schematic of the actual and equilibrium vapor pressure and temperature profiles given by equations 5.1a,b and 5.4 for a TDC chamber as a function of the chamber height and the resulting saturation ratio profile in the chamber as per equation 5.2.

Cloud condensation nuclei (CCN) are generally assumed to be composed of some form of sulfate (e.g., $(\text{NH}_4)_2\text{SO}_4$ or H_2SO_4). The following discussion of the prototype design is based on the assumption the instrument will be used to investigate hygroscopic $(\text{NH}_4)_2\text{SO}_4$ particles, although the approach described would be valid for any type of particle. $(\text{NH}_4)_2\text{SO}_4$ particles change from solid to liquid phase (deliquesce) at saturation ratios of less than 1 (i.e., at a relative humidity of 81% for $(\text{NH}_4)_2\text{SO}_4$ particles) when the Kelvin effect is negligible. To study the phase transitions of these particles it more useful to create humidities closer to the range where the phase transitions occur. Theoretically, the lower limit of TDC chamber humidity is the humidity at the endplates (Rogers and Yau, 1989). Thus, by lowering the saturation vapor density at the chamber end plates the vapor pressure profile throughout the chamber is correspondingly lowered. The solute effect (derived from Raoult's law) shows that the water vapor pressure over a wet surface can be lowered by adding an inorganic salt to the water (Seinfeld, 1986). Thus the relative humidity at the plates and throughout the chamber can be manipulated using filters soaked in an aqueous solution of an appropriate inorganic salt. This idea was used by Kocmond and Jiusto (1968) in their modified TDC in order to study fog properties. They used saturated solutions of KNO_3 to establish their relative humidities in their haze chamber. Different humidities can be obtained from different saturated salt solutions (see Table 5.1). Figure 5.3b is a phase diagram schematic comparing the saturation ratios generated in the chamber for water and for an aqueous salt solution.

aqueous salt solution.

Given plate temperatures T_1 and T_2 and the vapor pressures p_1 and p_2 of the aqueous salt solution on the filters at T_1 and T_2 , equation 5.4 can be used to calculate the saturation ratio at the chamber mid-point. For example, a relative humidity of 80% can be generated given plate temperatures of $T_1 = 25$ C, $T_2 = 20$ C, and an aqueous solution of NH_4Cl which has equilibrium water vapor pressures $p_1 = p(T_1 = 25 \text{ C}) = 18.84$ mm Hg and $p_2 = p(T_2 = 20 \text{ C}) = 13.94$ mm Hg. The theoretical saturation ratio profile as a function of height for our chamber is shown in Figure 5.4. Vapor pressures over various salt solutions are listed in Weast (1980).

5.2.2 Limitations of the TDC

The thermal diffusion chamber has been a popular instrument for studying cloud droplet populations and atmospheric aerosol activation into cloud, fog or ice particles. Despite its popularity and conceptual simplicity, it does suffer from some experimental difficulties. These difficulties are exacerbated by the TDC modifications made in order to develop the RITDC. The more significant limitations, temperature control, vapor supply, and particle separation distances are discussed in some detail below.

One of the assumptions made in TDC experiments is that the source of vapor at the chamber end plates is constant. In the prototype device discussed here, no provisions have been made to maintain the supply of liquid to the filters, and thus ensure a constant vapor supply. This could be an issue since the size of the particles in the prototype are large and take a long time (order of 30 minutes) to reach equilibrium size. For filters saturated with distilled water however, this gradual filter drying has a negligible effect on the experiments described in this chapter - the vapor pressure over the filters will still be the saturation vapor pressure over water so long as the filters are completely wet. In the case of filters soaked in saturated salt solutions, depletion of water content of the filters will change the ratio of salt to water on the filters. This in turn will lead to supersaturated solutions which have correspondingly lower saturation vapor pressures on the filters and, thus, lower saturation ratios at the midpoint of the chamber. To generate reproducible humidities in the chamber clean filters should be used for each experiment to ensure that there is no residual salt left on the filter which might change solution concentration.

Despite the potential difficulties in maintaining a constant vapor pressure at the RITDC endcap filters due to changes in salt solution concentrations, several experiments were successfully run to assess the feasibility of controlling water vapor pressure in the chamber using different aqueous salt solutions on the filters. Figure 5.5 shows typical results from one of these experiments. The curves show the

different vapor sources. (Increasing voltage corresponds to water uptake by the particles. Voltage is output from the refractometer part of the RITDC system which is described in the optical waveguide section.) Filters wetted with NaCl would be expected to generate lower water vapor pressures in the chamber than filters wetted with $(\text{NH}_4)_2\text{SO}_4$ while water-wetted filters would generate the highest water vapor pressures (See Table 5.1). The particles' rate of water uptake will increase with increasing amounts of water vapor. This is demonstrated in Figure 5.5. The particles do not appear to take up water when the filters are wetted with NaCl. This is to be expected because a saturated aqueous NaCl solution has an equilibrium vapor pressure over its surface corresponding to a relative humidity of approximately 75% (at $T = 298 \text{ K}$) while $(\text{NH}_4)_2\text{SO}_4$ particles deliquesce and grow at water vapor pressures corresponding to 81% relative humidity (at 298 K). When the filters are wetted with $(\text{NH}_4)_2\text{SO}_4$, a slow steady increase in voltage is observed, suggesting that the amount of water vapor present is right at the borderline concentration for which particle growth occurs. This is reasonable as the equilibrium vapor pressure over the filters soaked in a saturated solution of $(\text{NH}_4)_2\text{SO}_4$ is approximately the deliquescence humidity. Finally, in the case of the water-wetted filters, the particles grow quickly to an equilibrium size as they are exposed to water vapor pressures corresponding to relative humidities near 100%. Because the experimental results depicted in Figure 5.5 demonstrate the expected particle growth trends it seems reasonable that use of saturated salt solutions as water vapor sources will provide good control of the water vapor concentrations in the RITDC chamber.

One of the most difficult control issues with thermal diffusion chambers is control of the temperature at the end plates needed to create the thermal gradient in the chamber and thus control the relative humidity within a small range (approximately 5% span). This is typically done with either an array of thermoelectric modules and heat exchangers attached to each endplate or with a temperature-controlled liquid contacting each plate. Due to the difficulties of temperature control, the experiments discussed in this chapter relied solely on diffusion of vapor from the endplate filters and no thermal gradient. However a simple experiment demonstrating the influence of plate temperature on chamber conditions was done. The RITDC prototype's top plate temperature (T_1) was controlled by two thermoelectric modules (Teca Corp.) at temperatures approximately 3.4 and then 7 degrees greater than that of the bottom plate which was at room temperature. These temperature differences correspond to relative humidities of 100.5 and 101.9 respectively. (By keeping end plate temperatures near room temperature, the power required by the thermoelectric modules is minimized.) Digital temperature probes were used to monitor the temperature of the two plates. These results are compared with the results for no temperature control/thermal gradient in Figure 5.6 (V_{30} is the voltage at 30 min.). Figure 5.6 shows that, as expected, the particles in the thermal gradient pick up water faster and reach their equilibrium size sooner than the same particles with no temperature differential between the RITDC endplates. The question remains, however, as to whether this increased growth rate will be slowed by vapor depletion

from the filters with time or, even, if the increased driving force for diffusion will cause increase the rate of vapor depletion. A system to replenish/maintain the filters' source of water would eliminate this issue.

The RITDC is used to look at growth of multiple particles simultaneously. When dealing with multiparticle systems, vapor depletion by neighboring particles can influence the overall growth rate of the particles being studied. For high concentrations of particles it is assumed that there is a spherically symmetric vapor field around each spherical particle. Neighboring particles compete for the same vapor where their vapor fields overlap. This can be theoretically modelled using the electrical analogy of a potential field of a small sphere at the center of a spherical shell. Using the results of the analysis of Huffman and Vali (1973), the particles in the prototype RITDC ($d_p = 4 \text{ mm}$) would need to be approximately 4 cm apart in order for depletion of the vapor supply of their neighbor particles to be negligible. Fortunately, in the prototype device discussed here, the position of particles in the chamber is controlled (unlike traditional TDCs in which particles are randomly located with respect to each other). The particles can be placed wherever desired on the waveguide prior to the start of an experiment. However, for the large particles used in the prototype RITDC, it may be difficult to space them far enough apart that they do not influence the growth of other particles. Although it is not done in this work, by replacing the large glass rod waveguides with smaller waveguides such as optical fibers, smaller particles could be studied and the spacing between particles would be correspondingly less.

A simple experiment was performed to see if the influence of particle position was detectable in the prototype RITDC. On one waveguide, three particles were placed within 1 cm of each other, while on the other waveguide three particles were placed 4 cm apart. Water-wetted filters were used to generate a water vapor concentration in the chamber and the particle growth on the two wave guides was monitored. Figure 5.7 shows a typical result for this experiment. The particles spaced far (4 cm) apart on the waveguide grew more rapidly and reached their equilibrium size sooner than did the particles spaced close together (1 cm) on the waveguide. This qualitative result is in agreement with the idea that particles will compete for the same vapor and thus grow more slowly if they are located too close to each other.

In order to be able to investigate more than just trends and to acquire quantitative data from the RITDC the problems of temperature control and vapor supply must be addressed. In this pioneering, proof of concept study it does seem that the difficulties are surmountable. Even without well-controlled temperature and vapor in the RITDC, we are able to see some interesting trends and interpret them, keeping in mind the limitations of the current device.

keeping in mind the limitations of the current device.

5.2.3 Optical waveguide theory

Traditional TDCs are used to study the activation of relatively large populations of submicrometer particles to cloud droplets or ice crystals. Particles in this size range have low settling velocities and thus remain suspended in the chamber supported only by Brownian and diffusional forces. The particles are typically observed either photographically or by monitoring changes in light scattering due to changes in particle size. In this research, however, a smaller, controlled population of particles is observed at one time. The particles are supported at the chamber midpoint on 3 mm diameter glass waveguides and are several orders of magnitude larger (on the order of millimeters) than the particles typically studied in the TDC. Scaling down the waveguide (e.g., an optical fiber of 0.5 mm diameter) would permit the study of smaller particles with greater accuracy (this is discussed further in the future work section).

Changes in light transmission through the waveguides are detected by a photosensitive cell and are used to monitor composition changes of the particle. Qualitatively this works as follows: normally, the waveguide channels light from one point to the next with a minimum of light leakage. Light within the waveguide bounces against the waveguide walls but does not leak out if the index of refraction of the medium surrounding the fiber (e.g., air) is much less than the waveguide's index of refraction. If an aqueous salt particle is placed on the surface of the waveguide and begins to crystallize, its refractive index gradually increases to that of the crystalline salt. The index of refraction of salt is close to the index of refraction of glass and, thus, the salt particle acts as an extension the waveguide and some light will be diverted out of the waveguide through the drying particle. Light that leaks out is not transmitted to the other end of the waveguide and thus, the light power that is transmitted decreases.

An important parameter of a waveguide system is the critical angle. Light rays incident on the waveguide walls at angles greater than the critical angle will undergo total internal reflection and will be confined within the waveguide. Rays incident at angles less than the critical angle will not be totally internally reflected, and some fraction of the ray's power will leak from the waveguide. Figures 5.8a,b show this schematically. The critical angle is defined by:

$$\theta_{\text{critical}} = \sin^{-1} \left(\frac{n_{\text{outside}}}{n_{\text{waveguide}}} \right) \quad 5.5$$

where n_{outside} and $n_{\text{waveguide}}$ are the indices of refraction of the surrounding medium and the waveguide, respectively (Hecht, 1988). This equation shows that as n_{outside} increases, the critical angle increases.

transmitted by the waveguide to decrease.

A power balance on the light power in the system can be used to relate P_{transmit} to P_{loss} (Hecht, 1988):

$$P_{\text{in}} = P_{\text{transmit}} + P_{\text{loss}} \quad 5.6$$

where P_{in} is the power into the waveguide, P_{transmit} is the power transmitted to the other end of the waveguide, and P_{loss} is the power lost through the waveguide walls due to light leakage. If P_{in} is constant and P_{loss} changes due to changes in index of refraction of the surrounding medium, then P_{transmit} can also be related to changes in the index of refraction of the surrounding medium. This principle has been used for almost 40 years (Kapany and Pike, 1957) to create refractometers - instruments for measuring the index of refraction of liquids.

The basic refractometer consists of a waveguide, a light source, and a photo-sensitive cell (Figure 5.9). Sensitivity to index of refraction changes can be increased by modifications to the various components. For example, some refractometers have utilized bent or tapered waveguides (Bobb et al., 1988). The bend or taper increases the angular spectrum of incident light at the waveguide measurement site and makes changes in index of refraction easier to detect. The disadvantage of such a taper or bend is reproducing the exact same shape in each waveguide. Untapered glass rods are used in these experiments. With more sophisticated optics than are used in this research (e.g., a fiber optic system) bent or tapered waveguides might add an additional level of sensitivity to RITDC measurements.

Another way to adjust refractometer sensitivity is the choice of light source type. Either a diffuse (e.g., a lightbulb) or collimated (e.g., a laser) light source can be used to inject light into the waveguide. If a diffuse light source is used, light rays with a full range of incident angles are injected into the waveguide. This allows the determination of a large range of refractive indices. Another advantage of a diffuse light source is that alignment with the waveguide is not critical. A collimated source injects rays with a single incident angle. The advantage of this is that an angle can be chosen that maximizes sensitivity at a specific index of refraction allowing one to "tune" the refractometer. For simplicity a diffuse light source is used in these experiments.

5.3 THE RITDC APPARATUS

Table 5.2 lists the equipment used for the prototype RITDC. A schematic of the RITDC is shown in Figure 5.10. Changes in the light transmitted through the glass rod are measured and used to determine the index of refraction of the surrounding medium. The equation for determining the power of light transmitted through the waveguide for a perfectly diffuse source is (Snyder and Love, 1983):

$$P = I_0 \left(\frac{\pi}{n_{\text{end}}} \right)^2 (n_{\text{waveguide}}^2 - n_{\text{outside}}^2) r^2 \quad (5.7)$$

where P is the power of the transmitted light, I_0 is the intensity of the source per area, n_{end} is the refractive index of the medium between the waveguide and the lightsource, $n_{\text{waveguide}}$ is the refractive index of the waveguide, n_{outside} is the refractive index of the medium of interest surrounding the waveguide (i.e., in our case, a dry salt or aqueous particle), and r is the radius of the waveguide. We wish to compare the power transmitted when the surrounding (outside) medium is a salt particle or solution (P_{salt}) to the power transmitted when the surrounding medium is air (P_{air}). Taking the ratio of P_{salt} to P_{air} we get (Bobb et al., 1988):

$$\frac{P_{\text{salt}}}{P_{\text{air}}} = \frac{(n_{\text{waveguide}}^2 - n_{\text{salt}}^2)}{(n_{\text{waveguide}}^2 - n_{\text{air}}^2)} \quad (5.8)$$

Solving for the index of refraction of the salt particle or aqueous solution and using $n_{\text{air}} = 1$ we get:

$$n_{\text{salt}}^2 = n_{\text{waveguide}}^2 - \left(\frac{P_{\text{salt}}}{P_{\text{air}}} \right) (n_{\text{waveguide}}^2 - 1) \quad 5.9$$

Equation 5.9 yields a linear plot of the square of the index of refraction of the salt or salt solution as a function of the normalized power of light transmitted.

Figure 5.11 is a flowchart of how this experiment is used to determine particle growth rates. Through a series of calculations the output of a photocell, which is related to the power of light transmitted through the waveguide, can be converted to a relative mass (M/M_0). Because power transmitted is measured as a function of time, relative mass change with time (i.e., growth rate) can be calculated.

5.3.1 Proof of concept

The feasibility of observing changes in particle composition based on light transmission through a supporting glass waveguide ($n_{\text{waveguide}} = 1.47$) was tested. A glass rod (length = 254 mm, diameter = 3 mm) was aligned so that a diffuse light shone along its long axis. The light was detected at the other end of the rod using a Radio Shack cadmium/sulfide photo-sensitive cell (see Figure 5.9). A solution of ammonium sulfate and water was dripped onto the rod and allowed to dry in normal laboratory conditions ($T \sim 20^\circ\text{C}$, $\text{RH} \sim 30\%$). Qualitatively, a change in light transmission was visually noted by observing that the amount of light scattered by the crystalline coating the rod was much greater than the light scattered by the liquid solution on the rod. This scattering effect is illustrated schematically in

Figure 5.12. The output of the photo-sensitive cell ($m\Omega$) was converted into volts which were recorded and plotted with time. Figure 5.13a is a plot of voltage for a salt drop which is cycling through both crystallization and deliquescence as the humidity is changed in the chamber. As the salt solution crystallizes (dry data) the absolute value of voltage across the photocell decreases, indicating that less light is arriving at the photocell's light sensitive surface. The opposite effect is observed as the particle picks up water (wet data). Figure 5.13b shows the calculated index of refraction of the particle as a function of time which was determined using the procedure described in Figure 5.8.

5.3.2 RITDC calibration

The RITDC apparatus needs to be calibrated so that results such as those depicted in Figure 5.13 can be made more quantitative. There are two complementary basic methods of calibration. Calibration of the light-detecting photo cell is done using a series of neutral density filters to relate known amounts of light transmitted to the output of the photo cell. Calibration of the RITDC's response to changes in particle refractive index is done using liquids with known indices of refraction (e.g., glycerol/water solutions of known composition). Other system characteristics must also be investigated in order to obtain a quantitative understanding of experimental results. Specifically, the influence of particle size and the effect of an organic coating on the salt particle on the amount of light transmitted through the waveguide need to be considered. (Note: in the following discussion, the current prototype RITDC chamber holds two 3 mm glass rods serving as waveguides - in the plots they are referred to as blue and green, corresponding to their pen colors on the chart recorder.)

Figure 5.14a is a sample calibration plot showing voltage as a function P/P_0 for the two waveguides in the RITDC system. This plot was generated using a series of neutral density filters (Ealing #35-57xx) to change P/P_0 by attenuating a known fraction of the light incident on the waveguides and measuring the corresponding voltage at the light detectors. Figure 5.14a shows that the curves are quite linear in the range from $32\% < P/P_0 < 79\%$. In this range, then, relating measured voltage to the power of the transmitted light is simply a matter of using a linear curve fit to the calibration curve. (A more complicated curve fit can be used for measured voltages outside that range (e.g., Figure 5.14b).) The P/P_0 calculated from calibration curves such as these can be used in Equation 5.9 to solve for the index of refraction of the medium surrounding the waveguide.

Figure 5.15a shows several curves relating index of refraction of various glycerin-water solutions to P/P_0 . The legend labels (blue1, green1, blue2, green2) indicate which waveguide (blue or green) and which experimental run (1 or 2). The data presented in this figure were collected by placing a single drop of a glycerin-water solution with known index of refraction on the wave guide and recording the corresponding voltage at the light detector. A calibration curve was used to determine P/P_0 . Table 5.3

lists the composition of the various glycerin solutions and their corresponding index of refraction. Qualitatively, Figure 5.15a clearly displays the expected trend of decreasing light transmission with increasing glycerin concentration (i.e., increasing index of refraction). Quantitatively, however, the absolute values of power transmitted as a function of glycerin concentration are not very reproducible. P/P_0 varies by up to 20% for a given glycerin concentration. Reasons for the differences between observed and predicted values are discussed in the next section.

Figure 5.15b is a plot of observed versus predicted indexes of refraction for glycerin/water solution drops of varying composition. The observed value was calculated using equation 5.9 based on measured light transmission through the waveguide, while the predicted index of refraction was assumed known based on the composition of the glycerin/water solution and the values listed in Table 5.3. It can be seen in Figure 5.15b that the relationship between predicted and measured index of refraction is not 1:1, rather the experimentally determined index of refraction is always lower than the predicted index of refraction. Additionally, Figure 5.15b suggests that the number of drops on the waveguide may influence the experimental measurements.

5.3.3 Limitations of refractometer apparatus

There are several possible explanations for the observed variations of experimental measurements with the predicted values. Inhomogeneities in the solution droplets could change the index of refraction of the solution droplet next to the waveguide. Reading the voltage on the chart recorder is prone to human error. Finally, the size of the droplet and the way it is attached to the waveguide may result in different amounts of light scattering because the amount of scattering can depend on the amount of coverage of the waveguide. This last point is discussed in more detail below.

Equations 5.7 - 5.9 are based on the assumption that the waveguide is completely covered by the outside medium, i.e., air or solution droplet. In the experiments described here, the diameter of the particle being studied is much smaller than the length of the waveguide and thus only covers a small fraction of the waveguide. Therefore it is necessary to understand the effect of different amounts of waveguide coverage on the amount of light transmitted through the waveguide. The influence of coverage can be investigated both experimentally and theoretically. Experimentally, either droplets of different sizes or a number of droplets of the same size can be placed on the waveguide in order to observe differences in P/P_0 due to differences in waveguide coverage. Figure 5.16 shows voltage as a function of the number of droplets (100% glycerin, 64% glycerin, and water) placed on the waveguide. The amount of light transmitted continues to decrease with each droplet up to 10 or 11 droplets and then levels off as additional droplets are placed on the waveguide. This leveling off results when all of the light that can be lost from the waveguide is lost and thus, is equivalent to complete surface

coverage of the waveguide by the solution. Figure 5.16 agrees qualitatively with theory because it shows that as the concentration of glycerin (and thus the index of refraction) increases, the amount of light transmitted through the waveguide decreases (similar to what is shown in Figure 5.15a).

Theoretically, the amount of light lost through a particle sitting on a waveguide is related to the number of times the light ray strikes the waveguide/particle interface. Light striking the walls of the waveguide at an angle θ_{inc} is reflected back into the waveguide and/or lost from the waveguide depending on whether the incident angle is larger (reflected) or smaller (lost) than the critical angle (see Figure 5.8a,b). The presence of a particle on the waveguide increases the critical angle of the waveguide system and makes light loss from the waveguide more efficient. As more particles are added to the waveguide surface, the area with efficient light loss increases. By looking at the total number of times a light ray strikes the walls of the waveguide and considering the efficiency with which light is reflected at the waveguide/particle interface, the amount of coverage of the waveguide for maximum light loss can be estimated. The experiments described here utilize a diffuse light source, and thus there is a wide range of θ_{inc} . The light that will be lost from the waveguide most efficiently is the light with the smallest θ_{inc} . As θ_{inc} increases and approaches the critical angle θ_c the amount of light reflected back into the waveguide is greater and less light is lost from the waveguide. Thus, by considering the reflectance of at the waveguide walls at various θ_{inc} close to θ_c for different media surrounding the waveguide and by knowing the number and size of droplets, the influence of the amount of coverage can be determined.

If the waveguide has a length L_{wg} and diameter D_{wg} , then the number of reflections, N (equivalent to the number of times light hits the waveguide/outside interface), a light ray undergoes as it traverses the length of the waveguide is given by (Hecht, 1988):

$$N = \frac{L_{wg} \sin \theta_{inc}}{D_{wg} \cos \theta_{inc}} \pm 1 \quad 5.10$$

(rounded up to the nearest whole number). The number of reflections per particle (N_p) is simply $N_p = N (d_p/L_{wg})$ where d_p is the particle diameter. Table 5.4 lists the number of reflections for the waveguide for several incident angles calculated using equation 5.10. As the incident angle increases the number of reflections decreases. For the system being studied here, the particles are typically about 3 or 4 mm in diameter which corresponds to one reflection/particle. As can be seen from equation 5.10, the number of reflections per droplet increases with decreasing waveguide radius, thus scaling down to fiber optic size waveguides and correspondingly smaller particles should not create measurement problems for the RITDC.

Reflectance is defined as the ratio of reflected light power to incident light power at an interface. Reflectance at an interface can be calculated as a function of incident angle using the Fresnel equations (see Hecht (1988) or any optics text for details). Figure 5.17 shows reflectance as a function of incident angle for waveguide/air, waveguide/water, and waveguide/glycerin interfaces. For most incident angles less than the critical angle, light is very efficiently lost from the waveguide, i.e., reflectance is small. At angles approaching the critical angle reflectance increases, and it is for this range of angles that the amount of coverage of the waveguide influences P/P_0 . In an optical system, reflectance as a function of the number of reflections N is found using $R_{sys} = R^N$. Combining the information used to plot Figure 5.17 (i.e., reflectance as a function of incident angle) and knowing the number of reflections per particle N_p is approximate one, the reflectance is calculated for different numbers of droplets on the waveguide. This is the theory curve plotted in Figure 5.18. Also plotted on Figure 5.18 are experimental results (measured curve) for increasing number of water droplets on a waveguide. The shape of the measured and theory curves are quite similar. The small difference in the shape of the two curves is due to the fact that the reflectance was calculated for only one incident angle, whereas in the RITDC which utilizes a diffuse light source, reflectance would be integrated over the entire range of incident angles ($0 - \theta_c$). Thus the values for the theoretical and measured curves are not in complete agreement due to the use of a diffuse light source and also due to the approximation of the number of reflections per particle.

Every time an interface is added into the path of a light ray, an additional set of light reflection and transmission characteristics must be considered in order to track the light's behavior at each interface. This is depicted schematically in Figure 5.19 for both the uncoated and coated particles on the waveguide. Thus, the organic coating on the salt particle may influence the amount of light transmitted through the waveguide by creating another interface at which light can both leak from the salt particle and be reflected inward back into the waveguide. This effect depends on the thickness and refractive index of the organic coating. However, for the RITDC experiments discussed here, the potential for reflection back into the waveguide is ignored for both the uncoated and coated salt particles. Once light leaks out of the waveguide into the salt particle it is assumed it will not reflect back into the waveguide. It is assumed that the organic contacts the surface of the salt only and does not come into contact with the waveguide. It is also assumed that the organic does not react with the salt.

Another issue to consider is the degree of inhomogeneity of the particles. A particle undergoing deliquescence or crystallization will simultaneously consist of liquid and solid phase portions. The appropriate index of refraction of such a mixed phase inhomogeneous particle is less readily identifiable than the index of refraction of a homogeneous particle. The RITDC will not yield quantifiable data for

than the index of refraction of a homogeneous particle. The RITDC will not yield quantifiable data for such particles, although the phase change itself will be obvious.

From the above discussion it appears that the major limitation of the RITDC apparatus is reproducibility of waveguide coverage. Variations in particle size can have a large influence on measured light transmission. One possible solution to avoid the problem is to use a microsyringe to place the aqueous droplets on the waveguide and thus ensure they are all the same volume.

Unfortunately, due to the random nature of the crystallization process, combined with the large size of the particles, as the particles undergo crystallization they spread out on the waveguide support. This spreading results in different amounts of coverage contributed by each particle, even if the particles were all the same size when they were initially placed on the waveguide. For non-deliquescent/efflorescent particles this spreading effect is not an issue because the particles will remain in droplet form for the duration of the experiment, although the size changes associated with water uptake/loss must be included in calculations.

5.3.4 Summary of RITDC development

In this chapter it has been shown that the current RITDC prototype provides a feasible method for tracking phase change and particle growth. The prototype's potential environmental control ability has been tested and its optical systems have been characterized. This characterization work has suggested improvements to the RITDC system. In particular, environmental control in the chamber needs to be improved and tuned to desired relative humidities. Additionally, a more sophisticated waveguide system (i.e., using fiber optic technology) would increase reproducibility and applicability to the atmosphere.

5.3.5 Proposed experimental procedure

The procedure for these competition experiments as follows:

1. suspend particles of different composition on two separate glass rods within the chamber (e.g., one particle could be coated and one uncoated with organic)
2. measure changes in light transmission through the two rods as a function of time as the humidity in the chamber changes
3. relate changes in light transmission to particle growth or evaporation.

Differences in light transmission characteristics for the two rods will be due to differences in composition of the particles. A proof of concept experiment was done using particles composed of NaCl on one waveguide and of $(\text{NH}_4)_2\text{SO}_4$ on the other waveguide. The results from this experiment are shown in Figure 5.20a. There are two things to note: first, in all cases, the NaCl particles changed more quickly than did the $(\text{NH}_4)_2\text{SO}_4$ particles. Secondly, looking at all the runs together, it can be

particles changed. This suggests there is competition for the available water and the more hygroscopic NaCl particles are successfully uptaking water and slowing the growth of the $(\text{NH}_4)_2\text{SO}_4$ particles. Figure 5.20b shows results for a similar experiment. In this case the filters were soaked with a saturated solution of $(\text{NH}_4)_2\text{SO}_4$ and the particles being studied were pure $(\text{NH}_4)_2\text{SO}_4$ on one waveguide and a mixture (approximately 1:1) of $(\text{NH}_4)_2\text{SO}_4$ and NaCl. Figure 5.20b demonstrates that the mixture of salts is more hygroscopic and grows at a lower humidity than the pure $(\text{NH}_4)_2\text{SO}_4$ as predicted in thermodynamic arguments by Wexler and Seinfeld (1991).

5.4 FUTURE WORK

5.4.1 Improvements to RITDC

One way of improving the accuracy of the RITDC device would be to utilize optical fibers as the waveguides instead of 3 mm diameter glass rods. Accuracy would be improved in several ways. First, optical fibers are intended for light transmission and are manufactured to be optically homogenous, with a well-characterized index of refraction. The glass rod currently in use as a waveguide is common Pyrex glass with no claims of optical quality. Second, a typical optical fiber diameter is about 0.3 mm, i.e., a tenth the diameter of the glass rod. Equation 5.10 shows that the number of reflections in the waveguide increases inversely with the diameter of the waveguide. Thus fewer and/or smaller droplets would be required in order to attain the maximum light efficiency removal. Furthermore, with the appropriate equipment, optical fibers can be easily linked to the light source and detector for maximum reproducibility and accuracy.

5.4.2 Potential applications of the RITDC

This chapter has described the RITDC as a simple method for investigating particle composition and growth in the lab, using the particle's refractive index as an indicator of composition. Because of the simplicity of the device and the generality of the optical principles involved, a RITDC-like technique could be used for other applications as well. Below some possible applications are discussed briefly.

One possible application of a RITDC-type set up is to investigate cloud or fog droplet composition. Collett et al. (199x) have shown that the composition of cloud droplets is a function of their size. They determined this using a 2-stage cloud droplet impactor to collect the droplets and then chemically analyzed the collected cloud water. Size segregation of the cloud droplets was done using teflon strands of two different diameters - the larger droplets impacted on the larger strands and the smaller droplets on the smaller strands. Potentially, a waveguide of each diameter could be installed in the collection device and used to monitor index of refraction of the impacting droplets. The obvious difficulty with this idea is the lack of control over the number and size of particles impacting on the waveguide. Additionally, a clean waveguide would be necessary for each composition measurement desired.

Another potential application of the RITDC optics is to use the device as a relative humidity monitor (Flagan, 1995). In this case, the waveguide would be coated with a thin layer of a substance with a known response to relative humidity, i.e., H_2SO_4 . Calibration of the system would enable the user to identify light transmission through the waveguide with the corresponding relative humidity. If the coating layer was thin enough and the waveguide system well-characterized (e.g., an optical fiber) near real time humidity measurements could be made. The response time would be limited by the speed of the coating/water interaction and not the actual instrumentation. Similarly, some sort of RITDC set up could be used to obtain time dependent concentration measurements in annular denuders.

5.5 CONCLUSIONS

The RITDC is an innovative technique with good potential for investigating particle/vapor interactions. It can be used to investigate refractive index/compositional changes of laboratory-generated particles, competitive growth by particles of different compositions and real-time humidity changes.

5.6 TABLES AND FIGURES

Table 5.1 Relative humidity over various saturated aqueous salt solutions at T = 20 C. (Kocmund and Jiusto, 1968)

<u>Inorganic Salt</u>	<u>Relative Humidity</u>
LiCl	15%
CaCl ₂ ·6H ₂ O	32%
NaCl	75%
(NH ₄) ₂ SO ₄	81%
KNO ₃	94%
CaSO ₄ ·H ₂ O	98%
water	100%

Table 5.2 Equipment used for prototype RITDC apparatus.

<u>Function</u>	<u>Manufacturer</u>	<u>Model#</u>
Diffuse light source	Fiber Lite	3100
Chart recorder	Linseis	L 6514
Light detector (photocell)	Radio Shack	276-1657
Waveguide	Corning	Pyrex 3mm glass rod
Neutral Density Filters	Ealing	#35-57 series
Thermal electric modules	Teca Corporation	950-71
Power supplies for TEMS	BK Precision	1630

Table 5.3 Index of refraction of air, Pyrex glass, and water/glycerin solutions (Weast, 1980).

<u>Solution Composition</u>	<u>Index of Refraction</u>
air	1.00
Pyrex glass	1.474
water	1.33
24% glycerin	1.36
44% glycerin	1.39
64% glycerin	1.42
84% glycerin	1.45
100% glycerin	1.47

Table 5.4 Calculated number of reflections for RITDC waveguide for various incident angles.

<u>Incident Angle (θ_i)</u>	<u>Number of Reflections</u>
40°	101
60°	49
80°	15

Figure 5.1 Relative mass as a function of time for pure NaCl and for NaCl particles coated with octanoic acid exposed to a relative humidity of ~75% (from Andrews et al., 1993).

Figure 5.2 Cross-section of traditional thermal diffusion chamber.

Figure 5.3a Schematic of temperature and vapor profiles as a function of height and the resulting saturation ratio in a TDC i) linear temperature and vapor profile induced by temperature differential ii) vapor profile as a function of temperature based on the Clausius-Clapeyron equation iii) resulting saturation ratio profile.

Figure 5.3b Schematic of phase diagram of haze chamber principle comparing vapor pressure curve as $f(T)$ for salt and water (from Kocmund and Justo, 1968).

Figure 5.4 Theoretical relative humidity profile for prototype RITDC assuming NH_4Cl salt solution on filters and 5 K temperature difference between plates.

Figure 5.5 Relative humidity control in RITDC using various salt solutions on top and bottom filters.

Figure 5.6 Plot of normalized voltage as a function of time for various T differences between plates. Theoretically, $\Delta T = 0$ corresponds to $S = 1.0$; $\Delta T = 3.4$ corresponds to $S = 1.005$; $\Delta T = 7$ corresponds to $S = 1.019$. (Filters soaked in water)

Figure 5.7 Voltage (related to light transmitted) as a function of time showing differences in growth rate for particles spaced close to and far from each other on waveguide.

Figure 5.8a,b Loss and reflection of light rays at a waveguide interface: (a) total internal reflection (b) loss through the waveguide/air interface.

Figure 5.9 Schematic of refractometer apparatus.

Figure 5.10 Schematic of cross-section of RITDC apparatus.

Figure 5.11 Flowchart detailing relation between light transmission and relative mass change with time for particle in RITDC.

Figure 5.12 Schematic of light scattering out of light rod at particle/rod interface.

Figure 5.13 Voltage as a function of time for a salt drop which is cycling through both crystallization and deliquescence.

(a)

(b)

Figure 5.14 a) Sample calibration plot showing voltage as a function of P/P_o for the two waveguides in the RITDC system. b) Linear section of calibration plot showing voltage as a function of P/P_o .

Figure 5.15a Comparison of predicted and observed refractive index of various glycerin-water solutions.

Figure 5.15b Experimental curves relating refractive index of various glycerin-water solutions to P/P_0 .

Figure 5.16 P/P_0 as a function of water, glycerin, and glycerin/water droplets placed on the waveguide.

Figure 5.17 Reflectance as a function of the incident angle for waveguide/air, waveguide/water and waveguide/glycerin interfaces.

Figure 5.18 Theoretical reflectance compared with measured transmittance.

Figure 5.19 Schematic illustrating reflection/transmission at multiple interfaces. Dashed lines indicate reflected rays, solid lines indicate transmitted rays.

Figure 5.20a Comparison of growth for particles of different composition: for the same relative humidity conditions, NaCl particles tend to grow more quickly than do the $(\text{NH}_4)_2\text{SO}_4$ particles in the RITDC.

Figure 5.20b Comparison of growth rates for particles of differing composition at $RH_{\text{max}} = 81\%$.

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CHAPTER 6

CONCLUSIONS

6.1 INTRODUCTION

For this thesis, fundamental research was performed with the aim of understanding vapor scavenging in gas-particle systems relevant to the atmosphere. The influence of particle composition on vapor-particle interactions was explored through modelling and experimental work. Parameters which influence the evolution of aerosol size distribution were determined using computer simulations and investigated in a laboratory setting. In the experimental work, water vapor interactions with organic, inorganic and mixed particles were studied to determine vapor competition characteristics and particle hygroscopicity. It is important to understand gas-particle interactions because these interactions have the potential to alter a particle's characteristics (e.g., size, shape, composition, and/or phase) and thus influence the particle's behavior in the atmosphere. For example, particle transport, residence time and light scattering properties can be related to particle characteristics.

Observations have suggested that atmospheric particles composed at least partially of organic may contribute to CCN populations (Novakov and Penner, 1993; Rivera-Carpio et al., 1995). Other studies have analyzed the hygroscopic characteristics of organic-containing particles and found that the presence of organic may increase or decrease the water uptake properties of particles (Saxena et al., 1995; Ray and Pole, 1995; Rood et al., 1993, Andrews et al., 1993). These studies plus the ubiquitous presence of organics in the atmosphere strongly suggest that organics may play a significant role in atmospheric processes. Thus, the research presented in this thesis has focused on the influence of organics on atmospheric particle growth. By investigating the interactions of common atmospheric particles and vapors and improving our understanding of particle characteristics and behavior, this research has resulted in information useful for atmospheric researchers and modellers. This chapter summarizes the research described in this thesis and provides a synthesis of the implications of the results for atmospheric processes.

6.2 SUMMARY OF RESEARCH

The research described here is aimed at answering questions about the interaction of vapors with particles and in relating a particle's history of gas-particle interactions to its fate in the atmosphere. Specifically, gas-to-particle conversion and competition for water vapor by particles is influenced by the chemical composition of the particles involved. By considering a small subset of organic and sulfate compounds (and water) as was done in this thesis, much insight can be gained into atmospheric processes. Chapter 2 described modelling efforts investigating sources of organic in a marine aerosol and demonstrated the sensitivity of an evolving size distribution to model parameters. Chapter 3 detailed experiments with the

electrodynamic particle balance and showed the influence of organic coatings on the hygroscopicity of inorganic and elemental carbon particles. Chapter 4 analyzed the applicability of electrodynamic balance results to atmospheric systems with respect to particle charge and size. Chapter 5 described the RITDC prototype apparatus for investigating multiparticle growth in a controlled environment.

6.2.1 Summary of modelling work

A modified version of the MAEROS code was used to simulate the evolution of a marine aerosol size distribution. The simulations describe a general approach for use in determining potential sources of observed nucleation-sized organic aerosol. Specifically considered were two source scenarios, modelled with MAEROS, using system parameters that were adjusted until a good match with Novakov and Penners's (1993) observations was achieved. The parameter values used to match observations were examined and compared with literature data to see if the assumed values were reasonable. Although fairly good matches between the observed and simulated data for the assumed scenarios were achieved, one scenario could be ruled out based on the unreasonable values of the input parameters needed for the match.

This modelling study was also used to demonstrate the sensitivity of predicted number concentration to assumed input parameters. Development of initial conditions and input parameters brought to the fore the current lack of knowledge about organic and particle parameters in the atmosphere. The limited availability of measured/observed data in the literature suggested the need for considerable experimental work in order to obtain these necessary organic parameters. Two decades ago, the need to determine many organic parameters in order to model gas-to-particle conversion was noted (Heisler and Friedlander, 1977). Some of the parameters they cited included: gaseous diffusion coefficients, vapor pressures, density, solubility, activity coefficients and surface tension. Work in these areas is still necessary. This study suggested additional areas which would improve the modelling and characterization of the atmospheric aerosol: measurements of accommodation coefficients for a variety of atmospherically relevant species, vertical profiles of atmospheric constituents, homogeneity of the air parcel, organic speciation and the interplay amongst different organics and other atmospheric vapors.

6.2.2 Summary of electrodynamic balance work

The results from the electrodynamic balance experiments on carbon black particles coated with organic surfactants suggest that an organic coating increases the hygroscopicity of the ordinarily hydrophobic carbon black particles. These electrodynamic balance experiments showed that an ordinarily hydrophobic carbon black particle will sorb significant amounts of water (0.2 to 0.4 the dry mass of the particle) when the particle is coated with an organic surfactant such as Tween80 or azelaic acid. This phenomenon is especially interesting in the case of surfactants such as azelaic acid, which are themselves hydrophobic.

The electrodynamic balance is a good technique for studying aerosol systems of interest in the atmosphere as well as for a variety of other applications. It has been shown that particle charge does not influence experimental results in electrodynamic balance studies. Thus, the fact that the particles are charged does not affect the results' applicability to atmospheric systems. Comparison of TDMA and electrodynamic balance results show that extrapolating laboratory results to atmospheric particles greater than 0.5 μm diameter, is reasonable and the size of the laboratory particle is not likely an issue. Similar experimental results were obtained for pure particles in both electrodynamic balance and TDMA systems despite the two order of magnitude difference in particle size.

6.2.3 Summary of RITDC work

A prototype device, the refractive index thermal diffusion chamber (RITDC), for observing several particles of differing composition simultaneously, was developed and tested. The RITDC prototype provides an innovative and useful technique for investigating particle/vapor interactions. The RITDC combines the environmental control characteristics of the thermal diffusion chamber with the refractive index-based measurement technique used in a refractometer. By implementing suggested improvements and keeping in mind the device limitations, the RITDC has potential applications for investigation of compositional changes of laboratory-generated particles interacting with vapor; observation of competitive growth by particles of different compositions; and measurement of real-time humidity changes.

6.3 SYNTHESIS

Figure 6.1 is a schematic showing how the research in this thesis fits together and shows how each part of the research is necessary in order to get a fuller picture of how it relates to atmospheric processes. It is shown in Figure 6.1 that atmospheric particle modelling research depends on understanding fundamental processes both on the single particle level and for an array of particles. Additionally, modelling studies can show weaknesses in the knowledge base and, thus, focus experimental work. The modelling study described in this thesis showed that it is reasonable to expect natural organic vapors in the atmosphere to influence particle growth and size distribution evolution through gas-to-particle conversion. The MAEROS model identifies the mass of each species considered as a function of particle size, but in the interests of simplicity, lumps the species parameters (e.g., accommodation coefficient, density, etc.) into average system values for each size bin. Gas-to-particle conversion changes the mass concentrations in each size range, but the particle properties remain the same. Also, the size ranges affected depend on the type of gas-to-particle conversion (nucleation or condensation) which in turn is a function of the system parameters such as accommodation coefficient and initial particle concentrations. Because of this inter-relatedness and the fact that particle/vapor interaction parameters are lumped together (possibly obscuring fundamental processes), it is of interest to focus more narrowly on experimental vapor/particle system in order to identify

composition-dependent processes.

Single particle studies in the electrodynamic particle balance showed that mixed aerosol particles have different growth characteristics than single component particles. Additionally, it was seen that the growth characteristic of mixed component particles were not necessarily intuitive based on the behavior of the individual components. The observation that the presence of organic carbon in a particle can change a particle's ability to pick up water has several implications. It changes our understanding of what types of particles can participate in atmospheric processes such as cloud formation or precipitation scavenging. Further, it shows the importance of particle history on particle activity in the atmosphere. Finally, it suggests that in environments with limited vapor supply, the more hydrophilic particles will compete successfully for available water vapor and grow to equilibrium size at the expense of the less hydrophilic particles. To investigate what an array of different particles in the atmosphere would do in more detail the RITDC was developed.

The multi-particle RITDC experiments were a step back from the narrow single particle focus of the electrodynamic balance in order to look at the bigger picture by investigating how a population of particles of different compositions might grow in the same conditions/ air parcel. Due to calibrational complexity, the RITDC prototype has not yet been used investigate compositional dependent growth, although it is anticipated that those experiments would be straightforward, if the improvements recommended in Chapter 5 are made. Results from the RITDC apparatus would then complete the loop back to the modelling study by enabling the modeller to better understand the implications of ignoring compositional effects when modelling aerosol particles in the atmosphere.

The research in this thesis shows how particle history, structure (e.g., an organic coating) and composition are important parameters for determining particle growth. In particular, the presence of organic carbon in particles is shown to change the growth characteristics of the particles and, thus affect their ability to participate in atmospheric processes. These results suggest, then, that knowledge of particle history, structure and composition should be considered in atmospheric studies. This knowledge can be difficult to obtain, however, because the atmosphere is a complex system and there are many competing processes in the atmosphere. The advantage of laboratory and modelling research, such as that described in my thesis, is that a single parameter or mechanism can be studied in a controlled environment without the added complication of extraneous or compounded effects. In what follows, I discuss specific applications for particle growth results such as those acquired in my thesis research.

In a review article, Rogers and DeMott (1991) cite problem areas in atmospheric science for which an

improved understanding of particle growth would be useful. These areas include: global climate change, chemical processing in clouds and the influence of anthropogenic emissions on cloud processes. The issue of climate change is perhaps the area receiving the most attention currently. For example, the Department of Energy has an entire program (Global Change Research Program (GCRP)) devoted to elucidating uncertainties and quantifying effects of energy-related emissions on global climate change. In the 1993 DOE research summary report (DOE, 1993) the role of aerosol particles in various aspects of climate change was the focus of many of the research projects. For example, scientists are incorporating aerosol effects into most global circulation models (GCMs). As aerosol effects are incorporated into the models, the lack of information about aerosol chemical, physical, and optical properties is becoming clear (Quinn et al., 1995; Pilinis et al., 1995). This lack of information is the scourge of many modelling efforts - in this thesis the modelling with MAEROS was made more difficult because of unquantifiable parameter values. Furthermore, the model aerosol effects being implemented are based on sulfate aerosol parameterizations despite the fact that the global aerosol is composed of many species (e.g., soluble inorganics, water, organic and elemental carbon, and mineral dust). These different atmospheric constituents will behave differently, and recent work by Pilinis et al. (1995) demonstrates the importance of considering aerosol composition in climate models. They found that the most important parameter in modelling forcing by aerosols is changes in mass due to water vapor scavenging by aerosols (as was observed in my work). Growth due to water uptake is important because it changes the size, mass, index of refraction and scattering properties of the aerosol. For example, Pilinis et al. have shown that direct radiative forcing by atmospheric aerosols is strongly a function of the aerosol index of refraction and that a 5% change in refractive index can result in a 30% change in predicted climate forcing. By obtaining particle growth characteristics for a variety of atmospherically relevant constituents, and using these in combination with particle index of refraction calculations (e.g., Tang and Munkelwitz, 1994) more accurate forcing models can be developed.

Another area in which studies of particle growth are important is the determination of the relative influence of anthropogenic and natural sources of CCN active aerosol particles. Field work and modelling can be used to identify particle compositions and potential particle sources but it is also useful to quantify the water scavenging properties of the particles. Saxena et al. (1995) analyzed urban and rural aerosol observations and determined that the water content of atmospheric aerosols was influenced by the presence of organics. They found that presence of organic could have different net effects, e.g., organics lowered the hygroscopicity of urban aerosols but enhanced the hygroscopicity of rural aerosols. Saxena et al. suggested the need to obtain further information regarding the interactions between atmospheric organic species and water; in particular they cited the need for laboratory measurement of both the hygroscopic growth properties of water soluble organics and the hygroscopic behavior of inorganic species mixed with

hygrophobic and/or hygrophilic organics. Studies such as these were reported in this thesis and other works (e.g., Rood et al., 1993). Additional experiments on other atmospherically relevant species can be performed using the techniques described in my thesis work.

Chemical processing by clouds is another area of atmospheric research mentioned by Rogers and DeMott (1991). It is thought that cycling through a cloud system can alter the growth properties and thus the ability of different types of particles to act as CCN. This implies two levels of particle growth. For example, first a hygrophobic particle scavenges constituents which will make it hygrophilic. Second, the hygrophilic particle scavenges water vapor and becomes a cloud droplet. Cloud processing of aerosols can potentially influence rainfall events by changing the number and size distribution of the cloud droplet population (Rogers and Yau, 1989). Another implication goes back to the climate change issue: Chylek et al. (1984) investigated the influence of elemental carbon on the optical properties of clouds. They showed that the presence of an elemental carbon particle in cloud droplets changes droplet albedo and decreases the cloud reflectivity. Changes in cloud reflectivity will influence atmospheric radiative properties. Thus, investigation of the mechanisms which enable a particle (e.g., an elemental carbon particle) to scavenge water vapor, as well as the particle water scavenging rates themselves, will lead to a better understanding of atmospheric processing, transport and radiation.

The DOE report (1993) notes (with regard to climate change) that "the state of the science is that of incomplete model prediction and inconsistent observations". That comment is also applicable to the role that aerosols play in both global phenomena and more localized effects. The research described in this thesis provides knowledge and demonstrates techniques that will help in closing the gap between observation and prediction.

Figure 6.1 Schematic of three-pronged research approach indicating relation between MAEROS modelling, electrodynamic balance experiments, and RITDC experiments.

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APPENDIX A SAMPLE INPUT FOR MAEROS

```

1
1-forest simulation,4h
2-SECTIONS COMPONENTS #-OUTPUTS #-SOURCES STATUS nucbin pvap (kg/m3)
    30          2          1          2          1          30      5.5e-11
3-CONDENSE TP-TABLE NEWCOEF STORE AUTO-B INITIAL SOURCES FLAGNUC
    1          2          1          1          1          0          1          1.e-0
4-PLOTS PLOT-COMPONENTS ROWS COLUMNS MIN-CONC. MAX-CONC.
    1          1          20          50          0.          1.
5-CEILING/V FLOOR/V WALL/V CHI DIFFUSION-THICK DENSITY
    0.000      0.001      0.          1.          1.E-3          1500.
6-LEAK-RATE(m3/s) GAMMA STICK TG-C TG-F TG-W THERMAL COND. G/P
    0.00e-07      1.          1.e-00      0.          0.          0.          .05
7-RHO-C RHO-F RHO-W VFRAC-C VFRAC-F VFRAC-W VG-C VG-F VG-W
    1.E3 1.E3 1.E3 0.          0.          0.          0.          0.          0.
8-TURBDS VOL MW ROUND-OFF REL-ERR INIT VAP. r.h. ACC. COEF
    .0015      1      28.8 1.e-6      .003      5.5e-12      0.0      .0105
9-TGAS1 TGAS2 PGAS1 PGAS2
    298.      400.      1.E5      2.E5
10-SMALLEST-DIAMETER LARGEST-DIAMETER
    .00092257e-6      1.1718e-6
11-comp1-so4-(kg/m3) comp4-org
    0          0
    0          0e-28
    0          0e-28
    0          0e-28
    0          0e-28
    0          0e-28
    0          0e-28
    0          0e-28
    0          0e-28
    0          0e-28
    0          0e-28
    0.0e-28      0.0e-28
    0.0e-28      0.0e-28
    0.0e-28      0.0e-28
    5.2e-14      2.70e-13
    3.5e-13      3.43e-13
    1.7e-12      5.22e-13
    5.7e-12      5.12e-13
    1.4e-11      2.50e-12
    2.4e-11      0.55e-11
    3.1e-11      1.80e-11
    2.8e-11      3.3e-11
    2.5e-11      2.58e-11
    9.2e-11      0.35e-11
    3.2E-10      0.00e-11
    4.2E-10      1.02e-11
    2.0E-10      4.4e-11

```

	3.7181E-11	5.65e-11
	7.7848E-12	4.06e-11
	8.1509E-12	3.39e-11
	1.0255E-11	3.46e-11
12a-TIME	VAPOR-SOURCE-RATE (KG/S)/ AEROSOL SOURCE RATES (KG/S)	
0.	7.4-14	
.5e-14	.3e-6	1.3
1.5e-15	.5e-6	1.3
12b-TIME	VAPOR-SOURCE-gRATE (KG/S)/ AEROSOL SOURCE RATES (KG/S)	
43200	7.4e-14	
.5e-14	.3e-6	1.3
1.5e-15	.5e-6	1.3
EDIT AND OUTPUT TIMES (SECONDS)		
14400		
TIME	TEMPERATURE (K)	PRESSURE (PA)
0.	298.	1.e5
1.e6	298	1.e5


```

1
1-ocean simulation
2-SECTIONS COMPONENTS #-OUTPUTS #-SOURCES STATUS nucbin pvap (kg/m3)
    30          4          1          2          1          60          5.5e-11
3-CONDENSE TP-TABLE NEWCOEF STORE AUTO-B INITIAL SOURCESFLAGNUC
    1          2          1          1          1          0          1          1.e-0
4-PLOTS PLOT-COMPONENTS ROWS COLUMNS MIN-CONC. MAX-CONC.
    1          1          20          50          0.          1.
5-CEILING/V FLOOR/V WALL/V CHI DIFFUSION-THICK DENSITY
    0.000          0.0010          0.          1.          1.E-3          1500.
6-LEAK-RATE(m3/s) GAMMA STICK TG-C TG-F TG-W THERMAL COND. G/P
    0.00e-07          1.          1.e-00          0.          0.          0.          .05
7-RHO-C RHO-F RHO-W VFRAC-C VFRAC-F VFRAC-W VG-C VG-F VG-W
    1.E3          1.E3          1.E3          0.          0.          0.          0.          0.          0.
8-TURBDS VOL MOL-WT ROUND-OFF REL-ERROR INIT VAP. r.h. ACC COEF
    .0015          0.5          28.8          1.e-6          .003          5.00e-12          0.0          .00046
9-TGAS1 TGAS2 PGAS1 PGAS2
    298.          400.          1.E5          2.E5
10-SMALLEST-DIAMETER LARGEST-DIAMETER
    .00092257e-6          1.1718e-6
11-comp1,2,3-so4-(kg/m3) comp4-org
0          0          0          0
0          0          0          0
0          0          0          0
0          0          0          0
0          0          0          0
0          0          0          0
0          0          0          0
0          0          0          0
0          0          0          0
0          0          0          0
0          0          0          0
0          0          0          0
0          0          0          0
0          0          0          0
0          0          0          0
5.2e-14          0          0          2.7e-13
3.5e-13          0          0          3.43e-13
1.7e-12          0          0          5.22e-13
5.7e-12          0          0          5.12e-13
1.4e-11          0          0          2.5e-12
2.4e-11          0          0          .55e-11
3.1e-11          0          0          1.8e-11
2.8e-11          0          0          3.3e-11
2.5e-11          0          0          2.58e-11
9.2e-11          0          0          0.35e-11
3.2e-10          0          0          0.0e-11
4.2E-10          0          0          1.02e-11
2.0E-10          0          0          4.4e-11
3.7181E-11          0          0          5.65e-11
7.7848E-12          0          0          4.06e-11
8.1509E-12          0          0          3.39e-11

```

1.0255E-11	0	0	3.46e-11
------------	---	---	----------

12a-TIME VAPOR-SOURCE-RATE (KG/S)/ AEROSOL SOURCE RATEs (KG/S)

0	0.62e-15		
.3e-15	1.0e-6	1.3	
1.e-16	0.09e-6	1.3	
1.17e-15	0.3e-6	1.2	
0.7e-15	.62e-6	1.3	

12f-TIME VAPOR-SOURCE-gRATE (KG/S)/ AEROSOL SOURCE RATEs (KG/S)

1e8	0.62e-15		
.3e-15	1.0e-6	1.3	
1.e-16	0.09e-6	1.3	
1.17e-15	0.3e-6	1.2	
0.7e-15	.62e-6	1.3	

EDIT AND OUTPUT TIMES (SECONDS)

864000

TIME TEMPERATURE (K) PRESSURE (PA)

0.	298.	1.e5
1.e8	298	1.e5

APPENDIX B
INFLUENCE OF PARAMETER VARIATION ON ORGANIC
MASS DISTRIBUTION

Figure B.1 Influence of mixing height on simulated size distribution.

B.2 Influence of particle density on simulated size distribution.

Figure B.3 Influence of accomodation coefficient on simulated size distribution.

Figure B.4 Influence of nucleation diameter on simulated size distribution.

Figure B.5 Influence of organic vapor pressure on simulated size distribution.

Figure B.6 Influence of organic surface tension on simulated size distribution.

Figure B.7 Influence of nucleation tuner parameter on simulated size distribution.

APPENDIX C
VOLTAGE DIVIDER FOR RITDC APPARATUS

Figure C.1 Voltage divider for converting photocell resistance to dc volts.

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EDUCATION

1991-present Ph.D. Student, expected December, 1995 University of Illinois, Urbana, IL
Environmental Engineering and Science Program, Department of Civil Engineering
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1989-1991 M.S., May, 1991 University of Illinois, Urbana, IL
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Particles Using an Electrodynamic Balance*
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1985-1989 B.S., June, 1989 California Institute of Technology, Pasadena, CA
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PROFESSIONAL INTERESTS

Environmental engineering, air quality and aerosol physics, teaching and research

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1989-present Graduate Research Assistant, University of Illinois - *Designed and used
electrodynamic balance system and refractive index thermal diffusion chamber
for aerosol particle research.*

Spring, 1994 Student Guest, Lawrence Livermore National Labs - *Modelled organic aerosol size
distributions in order to determine possible sources of organic in observed marine
aerosol.*

May, 1993 Teaching Assistant, short course for International Atomic Energy Agency,
Argonne National Labs - *Prepared lab experiments and taught lab section.*

1991 Graduate Teaching Assistant, Air Resources Engineering, University of Illinois
Graded exams and assignments, held office hours.

1988 Summer Undergraduate Research Assistant, California Institute of Technology
Improved viewing mechanism for bubble-particle interaction experiments.

1986 Summer Laboratory Technician - California Institute of Technology
Prepared and deployed filter samples for Los Angeles basin field study.

HONORS, AWARDS AND ACTIVITIES

1993-present Membership in Sigma Xi, a scientific research honor society

1990-1995 Global Climate Change Fellowship awarded by the U.S. Department of Energy

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