MEASUREMENTS OF THE RATE AT WHICH SUBMICRON AEROSOL PARTICLES ARE SCAVENGED BY WATER DROPS

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Abstract—Experiments were performed to measure directly the rate at which submicron aerosol particles are collected by water drops. The scavenging drops were held stationary and the aerosol was passed slowly through the experimental chamber. Measurements were made on monodispersed particles of 0.03, 0.06 and 0.13 μm radius. The measurements were compared to theoretical predictions, which consider the effects of Brownian diffusion, thermophoresis and diffusiophoresis, and found to agree to within a factor of two.

INTRODUCTION

The lifetime and concentration of aerosol particles in the atmosphere depends on the rate at which the particles are attached to hydrometeors, since scavenging by precipitation is the major process by which aerosols are removed from the atmosphere (Junge, 1963). The rate at which aerosols are collected by cloud and precipitation particles is determined by scavenging processes which are dependent on the size of the aerosol particles. For large particles ($> 1.0\,\mu$m) inertial effects dominate the scavenging process; whereas for small particles ($< 0.1\,\mu$m) Brownian diffusion and the phoretic forces, thermophoresis and diffusiophoresis, dominate.

Realistic descriptions of the scavenging rate of aerosol particles are important for a variety of practical problems: predicting the lifetime and spread of aerosol plumes, describing the chemistry of contaminated clouds, designing techniques for aerosol removal, and predicting the rate and efficiency with which seeding material is incorporated into cloud droplets. Consideration of these problems among others has led to models which describe the rate at which aerosol particles are captured by hydrometeors.

Greenfield (1957) was the first to develop a model to calculate aerosol scavenging rates. More recently, models which include the effects of inertial capture and the phoretic forces have been developed by Slinn and Hales (1970) and Grover et al. (1977). Models considering Brownian diffusion and the phoretic forces have been developed by Slinn and Hales (1971), Young (1974), and Wang et al. (1978). Herbert (1978) developed a model which includes both the extremes of the inertial and the diffusive forces.

A number of experiments to measure the scavenging rate have been reported for aerosol particles and scavenger drops of a size where inertial effects are dominant (McCormack and Hilliard, 1970; Hampl et al., 1971; Kerker and Hampl, 1974); however, only a few measurements are available to compare with theory in the region where inertial effects may be ignored (Beard, 1974; Wang and Pruppacher, 1977). In addition, no experiments to measure the scavenging rate for aerosol particles less than 0.1 μm radius have been reported.

The purpose of this note is to report on the results of experimental measurements of scavenging rates using aerosol particles of 0.03, 0.06 and 0.13 μm radius. The experimentally measured collection kernels are compared with the theoretical model of Wang et al. (1978), with the difference that expressions for the phoretic forces in the 'transition regime' are incorporated into the model. Theory from the transition regime is used to describe the motion of particles of radius $> 0.006\,\mu$m and $< 0.2\,\mu$m for standard conditions of temperature and pressure.

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The experimental conditions and techniques employed here differ from the conditions and techniques used by other authors. The scavenging drops were mechanically suspended in a chamber to permit the long sampling periods required for the drops to scavenge a measurable quantity of particles (1–2 h). The long time periods were required because of the low scavenging rate, the small mass of the aerosol particles, and the low concentrations of monodispersed aerosol which could be generated. The monodispersed aerosol was passed through the chamber at a low velocity, to have minimal inertial collection. The aerosol particles were generated from a fluorescent dye and the scavenging rate was determined by measuring the fluorescence of the scavenging drops after a sampling period.

SCAVENGING THEORY

The forces which transfer aerosol particles to water droplets in the experimental arrangement under consideration are Brownian diffusion and the thermophoretic and diffusiophoretic forces. A theoretical expression for the collection kernel considering these forces has been obtained by Slinn and Hales (1971), Young (1974), and Wang et al. (1978). The collection kernel is defined as $K = J/N_0$, where J is the rate of particle flux to the scavenger and N_0 is the ambient aerosol concentration. The expression given by Wang et al. (1978) for the collection kernel can be written as

$$K = \frac{4\pi a^2 V_s}{\exp\left(\dfrac{V_s a}{D}\right) - 1}, \tag{1}$$

where D is the particle diffusion coefficient, a the radius of the collector drop, and V_s the sum of the velocities produced by the action of the phoretic forces. The derivation of equation (1) assumes spherical inverse square fields for the flux of heat, water vapor, and particles to the scavenger. While this is correct for stationary drops, modifications are necessary to describe these fluxes for droplets in a flow field. As a first-order correction for the effect of air motion mean ventilation coefficients were introduced by Wang et al. An expression for the forced convective ventilation coefficient for water vapor flux f_v is given by Beard and Pruppacher (1971). Following Wang et al. the functional form of f_v is also assumed appropriate for the ventilation coefficients for heat flux f_h and for particle flux f_p. The water vapor Schmitt number is replaced by the Prandtl number for f_h or the Schmitt number for f_p. Then the theoretical collection kernel is given by equation (1) with $V_s = f_v V_D + f_h V_T$ and $D = f_p D$. The phoretic velocities, V_D and V_T, are obtained from the product of the particle mobility with the phoretic force.

The forces controlling phoresis of an aerosol particle in a temperature gradient or a water vapor concentration gradient can be characterized by the Knudsen number, K_n, the ratio of the molecular mean free path of the gas to the aerosol radius. Three regimes are usually considered: (1) free molecule for $K_n \gg 1$, (2) transition, $K_n \sim 1$, and (3) slip flow, $K_n < 1$.

Correspondingly the expressions used to describe the phoretic forces depend on K_n. For standard conditions of temperature and pressure aerosol particles of approximately 0.006 to 0.2 μm radius are considered in the transition regime and neither the free molecule (particles < 0.006 μm) nor slip flow (particles > 0.2 μm) theories strictly apply (Brock, 1962). An expression for the thermophoretic force in the transition regime is given by Jacobsen and Brock (1965) and an expression for the diffusiophoretic force by Brock (1968). Combining these expressions with the Knudsen–Weber (1911) formula for the particle mobility, the following expressions are obtained.

The thermophoretic velocity

$$V_T = \frac{-16r\lambda e^{-\tau/K_n}\nabla T}{45\pi\eta\bar{v}}\left[1 + AK_n + BK_n e^{-C/K_n}\right],$$

where r is the radius of the aerosol particle, λ the thermal conductivity of the air, η the viscosity of the air, $\bar{v}$ the average molecular velocity of the gas molecules, T the temperature, A,

B, C, constants in the Knudsen–Weber formula, and τ an empirical parameter to fit the thermophoretic force from the free molecule theory to experimental observations made using a Millikan cell (Schmitt, 1959; Jacobsen and Brock, 1965). An expression for τ is given by Hidy and Brock (1970).

The diffusiophoretic velocity

$$V_D = \frac{-64\left(1 + \dfrac{\pi\alpha}{8}\right)}{45\pi K_n \gamma_D} D_{wv}\nabla\gamma_{wv}.$$

$$\left[\sqrt{\frac{M_w}{M_d}} - \frac{0.071}{K_n}\sqrt{\frac{2M_w}{M_w + M_d}}\right]\left[1 + AK_n + BK_n e^{-C/K_n}\right],$$

where D_{wv} is the water vapor diffusion coefficient, γ_d, γ_{wv}, the mole fractions of dry air and water vapor in the diffusing mixture, M_w, M_d the molecular weights of water and dry air, and α the molecular accommodation coefficient. A value of 0.9 has been used for α (Hidy and Brock, 1970).

Experiments using aerosol particles and scavenging droplets small enough that inertial effects can be ignored have been reported by Wang and Pruppacher (1977) and Beard (1974). The results of these experiments are shown in Fig. 1 along with calculations of the collision efficiency E for a range of humidities and scavenger drop radii. The collision efficiency is given by $E = K/(\pi a^2 V)$, where K is given by equation (1) and V is the terminal velocity of the scavenger. The results indicate reasonable agreement between theory and experiment. Inertial effects cannot be ignored for droplets of radius larger than 300 μm falling at terminal velocity and the comparison is truncated at that point. Wang et al. (1978) also found quite good agreement between their theoretical description and the experiments of Wang and Pruppacher (1977). The collection kernel of Wang et al. differs from equation (1) by using expressions for the phoretic forces from the theory in the slip flow regime.

EXPERIMENTS

The main components of the experimental apparatus are shown in Fig. 2. Water drops were suspended on wire supports in a chamber through which a monodispersed fluorescent aerosol was passed. At the end of a sampling period the water drops were collected and their fluorescence measured. An experimental measurement of the collection kernel K_e can then be
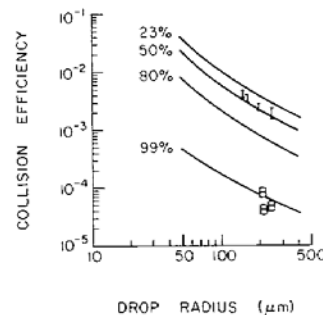

Fig. 1. Experimental results for aerosol particles of 0.25 μm radius, 23 % relative humidity, I (Wang and Pruppacher, 1977), and particles of 0.4 μm, 99 % relative humidity, B (Beard, 1974) compared with calculations of the collision efficiency, using equation (1) for the collection kernel. The curve for 99 % relative humidity is calculated for particles of 0.4 μm radius. The other curves are calculated for particles of 0.25 μm radius.
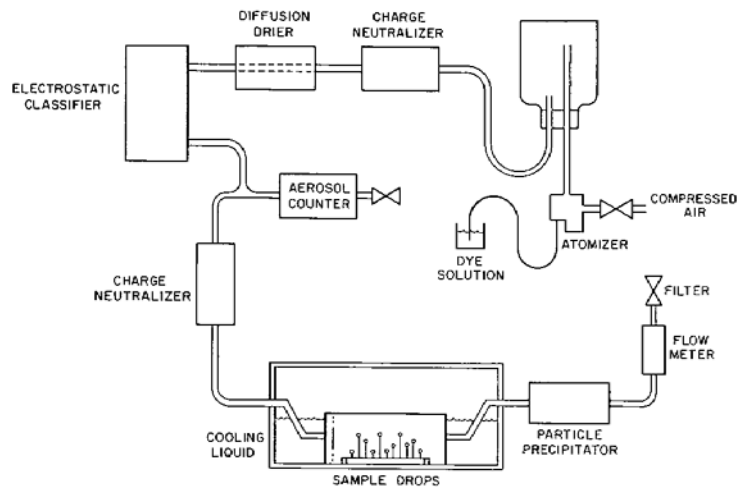
Fig. 2. Schematic of the sampling apparatus.

obtained from

$$K_e = \frac{C_d \rho_w}{t N_a \rho_d} \left(\frac{a}{r}\right)^3, \qquad (2)$$

where C_d is the concentration of dye in the sampling drops, t the time of sampling, N_a the aerosol concentration in the chamber during sampling, a is the average radius of the sampling drops, r the radius of the aerosol particles, ρ_d the density of the aerosol particles, and ρ_w the density of water.

The dye Rhodamine WT (Crompton and Knowles) was used to create the fluorescent aerosol. Since the density of the dye has not been reported it had to be measured. To do this a monodisperse droplet generator (Berglund and Liu, RNB Associates, Inc.) was used to create drops from a solution of known concentration. The drops were allowed to evaporate to a dry residue and the diameter of the residue was measured with a microscope. The density was then calculated from

$$\rho_d = C_s \rho_w \left(\frac{d_s}{d_r}\right)^3,$$

where C_s is the concentration of dye in the solution used to generate the drops, d_s the diameter of the solution drop, and d_r the diameter of the dry residue. The measurements were repeated using three different solutions. The average density from 26 measurements was $\rho_d = 1.57 \, \text{g/cm}^3 \pm 0.25$.

The fluorescent aerosol was generated by atomizing a solution of the dye and drying the solution drops. A monodisperse fraction of the aerosol was obtained using an electrostatic classifier (Thermo Systems, Inc.). The monodisperse fraction of the aerosol then passed through a charge neutralizer before entering the sampling chamber.

The number concentration of the monodisperse aerosol was measured using three techniques. First, the positively charged aerosol was sent to an absolute filter in a Faraday cage at a measured flow rate. A sensitive electrometer was used to measure the current generated by the aerosol flow, typically 0.2 to 2.0 pA. The aerosol concentration was then calculated by assuming each aerosol particle carried one elementary charge and applying a correction for the number of multiply charged particles which arise from an equilibrium bipolar charge distribution (Whitby and Liu, 1966). Second, an Aitken counter (Gardner

Associates, Inc.) was used. Third, the monodisperse aerosol was collected on a millipore filter, 0.45 μm pore diameter. Two filters were exposed in series at a measured flow rate. The filters were then rinsed in 10 ml of distilled water. The fluorescence of the rinse water was measured and the aerosol concentration calculated. Typically rinse water from the second filter in the series displayed no fluorescence. The concentrations measured by the filters and the electrometer agreed to within a factor of two. The Aitken counter however gave lower concentrations by a factor of 3–5.

Because of the agreement between the electrometer and the filter technique, and the ease of making the electrometer measurement, the concentrations measured by the electrometer were used for the calculation of the experimental collection kernel.

The aerosol concentration was measured at the start and end of each sample period and was quite stable. Variations of 5–25% were observed between the initial and final measurements. The average of these two measurements was used for the calculations. Monodispersed aerosol concentrations ranging from $2.8 \times 10^4/\text{cm}^3$ to $1.4 \times 10^5/\text{cm}^3$ were used for the experiments.

To confirm the size and to establish the size distribution of the aerosol samples used, the particles were collected on electron microscope grids. Either an electrostatic precipitator (Thermo-Systems, Inc.) or a thermal precipitator was operated on the outlet of the scavenging chamber during a sampling period. The microscope grids were then examined and photographed under a scanning electron microscope to determine a size distribution for each of the three monodisperse aerosol samples used. The dye particles displayed a nice spherical character. The aerosol samples were found to have a narrow size distribution, peaking very close to the size selected by the Electrostatic Classifier. The results are shown in Fig. 3. Each distribution is the result of sizing approximately 150 particles.
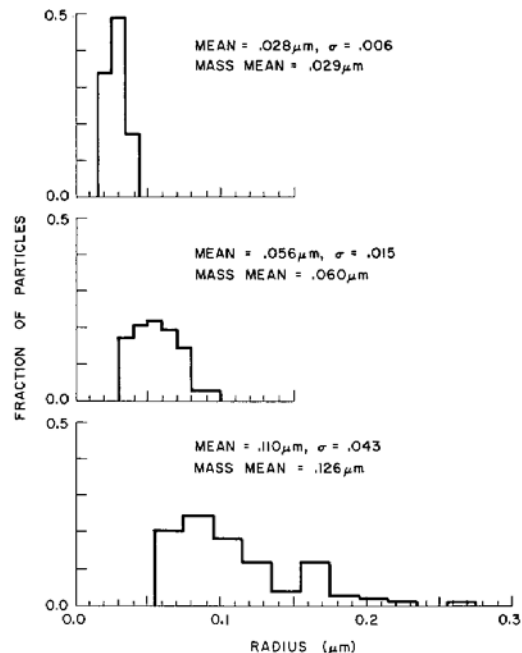

Fig. 3. Size distributions of the dye aerosol used for the measurements of the collection kernel. The mean and standard deviation of each distribution is shown. Also the radius corresponding to the average particle volume for each distribution is shown.

Before a sampling period was begun the sampling chamber was cooled to a temperature between -1 and $-2°C$. Sampling drops were then placed on the drop supports. This set of sample drops was removed immediately with a clean syringe and formed a background sample to measure the residual fluorescence of the drop supports, which was found to be negligible. A second set of sample drops was then placed on the supports and the chamber allowed to relax to equilibrium conditions. A monodisperse aerosol was generated, the concentration measured, and the aerosol was passed through the sampling chamber. The aerosol flow rate was measured at the outlet of the sampling chamber, and an aerosol precipitator was operated on the outlet. The sampling period depended on the mass and number concentration of the aerosol particles, but ranged from a half hour to two hours. At the end of the sampling period the aerosol concentration was measured again. The sampling drops were then removed with a clean syringe and placed in a microcuvette for the fluorescence measurement. The fluorescence of the samples was measured using a fluorometer (Turner) which had been calibrated with carefully measured solutions of the dye, Rhodamine WT, and distilled water.

Since the concentrations measured in the samples ranged from 1 to 100 ppb cleanliness was essential. New syringes were used for each set of sample drops. The microcuvettes were rinsed three or four times with distilled water and dried in a dessicator before reuse. Between runs each drop support was rinsed two or three times with a stream of distilled water. Background tests indicated that these precautions were adequate to keep the samples from being contaminated.

Knowledge of the radius of the sampling drops is essential for a calculation of the collection kernel from these experiments. The sampling drops were dispensed from a syringe in a device designed by the Atmospheric Science Department of the University of Wyoming, to produce a uniformly sized drop. The initial radius of the sample drop was 0.135 cm. Evaporation was accounted for in the course of a sampling period by measuring the mass of the sample removed and calculating the final radius of the sample drops. As a check the final radius of the sample drops was also calculated using an expression from Pruppacher and Klett (1978) for the evaporation rate of cloud drops. The calculated and measured radii agreed to within approximately 8% for the experiments conducted. For the calculation of the experimental collection kernel an average of the initial and final radius of the sample drops was used.

RESULTS

Eight experiments were done: two each using aerosol particles of volume mean radius 0.029 and 0.126 μm and four using aerosol particles of 0.060 μm radius. Humidity and temperature in the sampling chamber varied from sample to sample, but was constant throughout a sampling period. The humidity ranged from 60 to 97% while the temperature was between -1 and $-2°C$. The pressure was approximately 780 mb. The results of the measurements are shown in Fig. 4 compared with theoretical calculations of the collection kernel. The measured collection kernel was calculated assuming a monodispersed aerosol of radius equal to the volume mean radius of the slightly polydisperse aerosol sample used. The theoretical collection kernel was calculated for the appropriate experimental conditions and a range of aerosol sizes. For the different experiments the radius of the sampling drops ranged from 0.12 to 0.13 cm and the aerosol flow velocity ranged from 0.18 to 0.21 cm/s.

To account more fully for the slightly polydisperse character of the dye aerosol, the dye concentration expected in the sample drops was calculated from

$$C_d = \frac{t N_a \rho_d}{\rho_w a^3} \int K(r) f(r) r^3 \, dr,$$

where $K(r)$ is obtained from equation (1) and the distribution function $f(r)$ is determined from the size distributions shown in Fig. 3. The results are shown in Table 1.

The results of the two comparisons, Fig. 4 and Table 1, indicate that the theoretical and experimental collection kernels agree to within a factor of two. The uncertainties in the
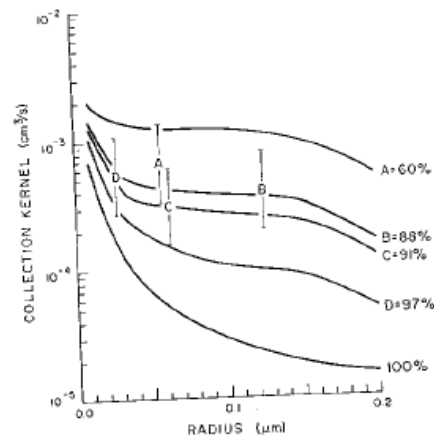
Fig. 4. Theoretical collection kernels for different humidities compared with measurements of the collection kernel made using a fluorescent aerosol. The letters display the average of two measurements at the humidities indicated, and are centered on the volume mean radius of the aerosol sample. The error bars represent the cumulative effect of uncertainties in the measurement of experimental quantities needed to determine the collection kernel.

measurement of the quantities used to obtain the experimental collection kernel range from 10 to 25%. The cumulative effect of these uncertainties indicates an experimental uncertainty of a factor of 2–3 in the experimental collection kernel. Thus the theory and experiment agree to within the uncertainty of the measurement technique.

SUMMARY AND CONCLUSIONS

Experiments were conducted to measure the scavenging rate of submicron aerosol particles by water drops. The measurements are compared with the theoretical scavenging rate which has been developed to account for the combined effects of Brownian diffusion, thermophoresis, and diffusiophoresis. The theoretical model developed by Wang et al. (1978) was used for comparison, although different expressions for the phoretic forces were included to describe these forces for the small aerosol particles used in this study. The experiments were done with low velocity flow in unsaturated air at temperatures near $-1°C$, and a pressure of 780 mb, using aerosol particles of 0.03 to 0.13 μm radius. The experimental conditions and the techniques used are quite different from previous experiments which have been reported. In particular no experiments have been reported which use aerosol particles < 0.1 μm. The

Table 1. Comparison of the experimental measurements with the theoretical dye concentrations calculated by integrating over the size distribution of the aerosol sample used

Aerosol radius Volume mean (μm)	Dye concentration (ppb) Calculated	Dye concentration (ppb) Measured	Ratio exper/theory
0.029	1.40	2.65	1.89
0.029	1.22	2.15	1.76
0.060	25.0	13.5	0.540
0.060	18.7	33.0	1.76
0.060	236.	91.5	0.387
0.060	157.	91.5	0.581
0.126	140.	162.	1.16
0.126	92.3	181.	1.96

measurements agreed to within a factor of two with the theory for this size range of aerosols, which was within the uncertainty of the experimental measurements.

Because of the wide range of conditions and particle sizes where theoretical scavenging calculations are employed, it is valuable to have a variety of experiments, covering a range of particle sizes, as a basis to check the theory. The experimental technique presented here could be extended to perform measurements on a wider range of aerosol sizes. It has been limited to small particles in this study due to the interests of the author. Although the experiments reported here are not exhaustive, it is felt they add an additional touchstone for users of theoretical scavenging calculations, in a size range and with a technique heretofore unexplored.

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