Observation of hydration of single, modified carbon aerosols

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Abstract. We have compared the hydration behavior of single carbon particles that have been treated by exposure to gaseous H₂SO₄ with that of untreated particles. Untreated carbon particles did not hydrate as the relative humidity varied from 0 to 80% at 23°C. In contrast, treated particles hydrated under subsaturation conditions; mass increases of up to 30% were observed. The mass increase is consistent with sulfuric acid equilibration with the ambient relative humidity in the presence of inert carbon. For the samples studied, the average amount of adsorbed acid was 14% ±6% by weight, which corresponds to a surface coverage of ~0.1 monolayer. The mass fraction of surface-adsorbed acid is comparable to the soluble mass fraction observed by Whitefield et al. (1993) in jet aircraft engine aerosols. Estimates indicate this mass fraction corresponds to 0.1% of the available SO₂ exiting an aircraft engine ending up as H₂SO₄ on the carbon aerosol. If this heterogeneous process occurs early enough in the exhaust plume, it may compete with homogeneous nucleation as a mechanism for producing sulfuric acid rich aerosols.

Introduction

Carbon aerosols play an important role in both chemical and radiative processes in the atmosphere. Although they comprise less than 1% of the total aerosol in the upper troposphere and lower stratosphere (Pueschel et al., 1992), they may dominate atmospheric radiative properties through their large absorption cross sections. Chylek et al. (1984) suggested that black carbon, either in the interior or on the surface of a cloud drop, can significantly change the albedo of the droplet and decrease the reflectivity of clouds at wavelengths less than 1 μm by as much as 20% over that of pure water for a soot volume fraction of 10⁻⁴. Although pure black carbon is hydrophobic and requires much higher supersaturations to activate than a hydrophilic material such as H₂SO₄ (Niessner et al., 1990), it is usually injected into the atmosphere in the presence of sulfur species during combustion. In fact, this observation forms the basis of the recent global inventory model for black carbon developed by Penner et al. (1993).

Although most sources of black carbon are ground based, carbonaceous aerosols are injected into the middle and upper troposphere by commercial and military aircraft. Interactions with sulfur-containing and other trace gases present in the exhaust plumes of aircraft could dramatically change the hydration properties of carbon particles. There is some controversy concerning the degree to which jet aircraft exhaust aerosols act as cloud condensation nuclei (CCN). Hudson et al. (1991) and Pitchford et al. (1991) measured the CCN/CN (CN, condensation nuclei) ratios for various jet fuels in both large controlled burns as well as actual aircraft plumes and typically found CCN/CN ratios of <1% at supersaturations of 1%. In contrast, Hagen et al. (1992) and Whitefield et al. (1993) sampled the exhaust of jet engines and of lean premixed, prevaporized burners and found CCN/CN ratios on the order of 30 to 40% at 1% supersaturation. On average, they found the aerosols contained 10% soluble material by weight.

The hydration behavior of a carbon particle is determined by the amount of soluble material it contains, which is determined by both the combustion and near field plume chemistries. The most likely water soluble candidate is sulfuric acid, although nitric acid may also be present. Recently Arnold et al. (1992 and 1993) measured enhanced levels of NO, NO₂, HNO₂, HNO₃, SO₂, SO₃, and H₂SO₄ in the plumes of commercial airliners at cruise altitude. They found that the H₂SO₄ levels were high enough to be supersaturated with respect to binary H₂SO₄-H₂O solutions. Depending on the distribution of H₂SO₄ between the soot particles and homogeneously nucleated sulfuric acid droplets, the fraction of carbon particles that act as CCN could be significant.

Another pathway for H₂SO₄ deposition on carbon aerosols is direct oxidation of surface adsorbed SO₂ to sulfates (Novakov, 1982). Water vapor enhances the oxidation process; it is not entirely clear whether this process is enhanced by other oxidants such as O₃ or NO₂ (Cofe et al., 1981, 1984; Baldwin, 1982). Thus, the aging of a carbon aerosol and its associated impurities can strongly influence the reactions that occur on it. In comparison, hydrophilic black carbon reduces NO₂ (Tabor et al., 1990) while hydrophilic black carbon oxidizes NO₂ to HNO₃ and HNO₃ via aqueous chemistry in adsorbed water (Gundel et al., 1989). Determination of the amount of adsorbed impurities required to change the nature of soot from hydrophobic to hydrophilic is important to accurately model heterogeneous chemical processes in the atmosphere.

A unique way to study many of the important chemical and physical processes involving single particles under well controlled laboratory conditions is with an electrodynamic balance (Arnold and Folan, 1987). This paper describes...
preliminary experiments using an electrodynamic balance to study the hydration properties of single untreated carbon spheres in comparison with spheres that have been treated with H₂SO₄. The experiments demonstrate that: 1) H₂SO₄ is readily adsorbed and retained on carbon spheres, 2) untreated spheres do not hydrate over the range of relative humidities (0 to 80%), and 3) treated spheres readily hydrate under subsaturated conditions and their behavior is consistent with hydration of pure acid in the presence of an inert substrate. The amount of acid adsorbed on the carbon particle averaged 14% ± 6% by weight, which corresponds to a surface coverage of ~0.1 monolayer. Finally, we estimate only 0.1% of the SO₂ exiting a typical jet aircraft engine needs to deposit on the emitted carbon soot as H₂SO₄ to produce activated carbon particles.

**Experimental Equipment and Procedures**

The electrodynamic balance used in these experiments, Figure 1, is a spherical void electrodynamic levitator (SVEL) composed of three electrodes: a central ring electrode which is biased with the AC trapping voltage and a pair of endcap electrodes which are biased with a DC voltage (Arnold and Folan, 1987). The trapped particle is illuminated with a HeNe laser. Light scattered at 90° is imaged using a microscope-based video camera and monitor. Since the DC voltage necessary to balance the particle against gravity is proportional to its mass to charge ratio, the relative particle voltage necessary to balance the particle against gravity is given by the particle mass and the applied current.

Figure 1, is a spherical void electrodynamic levitator (SVEL) controlled cell. The humidity of the gas entering the cell is controlled by passing it through a water saturator. A total gas flow rate of 100 sccm gives a reasonable cell equilibration time without perturbing the particle balancing voltage. The water activity or relative humidity (RH) in the trap is related to the flowrates and the temperatures in the system by:

$$\text{RH} = \frac{F_{\text{sat}}}{F_{\text{sat}} + F_{\text{bypass}}} \cdot \frac{P_{\text{sat}}(T_{\text{sat}})}{P_{\text{trap}}(T_{\text{trap}})}$$

where $F_{\text{sat}}$ is the flow of nitrogen through the water saturator, $F_{\text{bypass}}$ is the bypass flow, $P_{\text{sat}}(T_{\text{sat}})$ is the vapor pressure of water at the saturator temperature, and $P_{\text{trap}}(T_{\text{trap}})$ is the vapor pressure of water at the trap temperature. The accuracy of this method was verified by measuring the dew point of the mixed stream using an EG&G model 911 digital humidity analyzer. The two methods agreed to within 3 to 5%. Two calibrated T-type thermocouples are used to measure $T_{\text{sat}}$ and $T_{\text{trap}}$. The error in a relative humidity measurement is ±10%.

We used Spherocarb, a chromatography packing material, as the model black carbon aerosol. As we are concerned with processes that lead to particle activation, a logical black carbon aerosol with which to start is one that is free from impurities and well characterized in terms of size and surface area. Spherocarb is such a material; it is a high purity, porous synthetic carbon with a spherical shape. This choice allows us to remove any complicating behavior that might arise by comparing particles having different aging or processing histories. The activation mechanisms studied on this substrate material are likely to figure largely in the hydration behavior of combustion-generated black carbon aerosols. The particles used in these experiments were nominally 120/125 mesh corresponding to a diameter range of 125 to 150 μm. The particles had densities of 0.8 to 1.2 g/cm³ (Wong, 1991) and a BET surface area determined by N₂ adsorption of 864 m²/g (Waters, 1988). These particles are much larger than typical jet engine combustion aerosols (mean diameter ~0.035 μm) (Whitefield et al., 1995).

Particles were treated with H₂SO₄ by two different methods. In the first method, 2 ml of Spherocarb particles were mixed with 10 ml of high purity 97 wt% H₂SO₄ in a clean glass test tube. The test tube was placed in an oven overnight at 140°C to evaporate the excess sulfuric acid. In the second method, 2 ml of Spherocarb particles were placed on a watch glass inside a larger glass dish containing 10 ml of 97 wt% H₂SO₄, covered with a second watch glass and placed in the oven at 125 to 140°C overnight. This preparation method deposited H₂SO₄ onto the particles by vapor transport. Four separate batches of carbon particles were treated and studied.

For each experiment, a single Spherocarb was captured and balanced in the humidity controlled trap under ambient conditions. The initial balancing voltage, temperature, and ambient humidity were recorded. Dry N₂ flow was directed through the trap, and the particle equilibrated to its dry mass after 15 min. The dry balancing voltage was used to normalize subsequent measurements to derive relative mass gains. Balancing was performed manually by centering the particle image at the trap null point using the camera monitor. Balancing voltages were measured with an accuracy of 1%. After a step change in the relative humidity of 10 to 20%, the particle was allowed to equilibrate for 15 to 30 min before rebalancing.
Results and Discussion

The results from a typical particle growth experiment are shown in Figure 2 for an untreated particle and a particle treated by vapor deposition of H₂SO₄ at 140 °C. Untreated carbon particles did not gain or lose mass during these experiments. In comparison, treated carbon particles readily gained mass as the RH was varied; that is, they hydrated under subsaturated conditions. There was some variation in hydration behavior of the particles from different treatment batches.

If we assume the carbon is inert, we can use the thermodynamic equilibrium behavior of aqueous sulfuric acid (Zeleznik, 1991) to determine the relative mass of sulfuric acid adsorbed on the carbon from:

\[ \frac{y}{x} = \frac{C_2 - C_1 q}{C_2 - C_1 q} \]  

where \( y \) is the mass of acid, \( x \) is the mass of carbon, \( q \) is the ratio of the weights at RH₁ and RH₂, and \( c_1 \) and \( c_2 \) are the acid concentrations (wt%) of the aqueous sulfuric acid solutions in equilibrium with the corresponding relative humidities. Based on experiments with pure H₂SO₄ droplets, \( c_1 \) was found to be 80% at the lowest RH (0.3%) we could achieve in the apparatus. For the data of Figure 2, the value of \( y/x \) that best represents the data is 0.18, which corresponds to a soluble mass fraction of 15%. Soluble mass fractions were measured to be 14% and 15% for particles treated at 140°C and 6% and 21% for particles treated at 120°C. These results yield an average soluble mass fraction of 14% ±6% (1 sigma). Bulk analysis of one batch of H₂SO₄ treated carbon particles found S/C ratios three times larger than values deduced from the thermodynamic calculation. In this preliminary study, we cannot determine whether some H₂SO₄ is not available at the surface for hydration or if there is a change in speciation of some of the H₂SO₄ following adsorption.

Surface coverage (the number of monolayers of acid, ML) can be estimated as:

\[ ML = \frac{y}{x} \cdot \frac{N_A}{MW \cdot S \cdot N_M} \]  

where \( N_A \) is Avogadro's Number, MW is the molecular weight of H₂SO₄, S is the specific surface area of the carbon, and \( N_M \) is the number of molecules H₂SO₄/cm² corresponding to one monolayer coverage. A simple, close packed sphere model for H₂SO₄ gives \( N_M = 4.5 \times 10^{13} \) molecules/cm². With these assumptions, we estimate H₂SO₄ surface coverages of 0.1 to 0.3 monolayer for 10 to 22% soluble mass fractions. Since H₂SO₄ is larger than \( N_2 \), the apparent submonolayer coverage of H₂SO₄ may be a lower bound if the smallest pores accessible to \( N_2 \) in the BET measurements are inaccessible to H₂SO₄ during vapor deposition.

We next consider how the hydration behavior of our model system compares to black carbon aerosols emitted by jet aircraft engines. Recent field and test stand measurements by Whitefield et al. (1993) showed that soot particles have aerodynamic mean diameters in the range of 10 to 200 nm with a peak in the number distribution at 35 nm. Assuming a monodisperse aerosol with 35 nm diameter and a density of 1.9 g/cm³, an estimate for the specific surface area of the particles is 90 m²/g. This value compares well with commercial carbon blacks produced by combustion which have specific surface areas ranging from 100 to 1600 m²/g (Vermeulen et al., 1973). Based on the growth of both 34 and 49 nm particles, Whitefield et al. concluded that ~10% of the particle mass was soluble. If all of the soluble mass is H₂SO₄, this corresponds to a surface coverage of approximately 0.7 monolayer for the estimated specific surface area. These values for soluble mass fraction and surface coverage are similar to those observed in our experiments. This similarity implies that the black carbon is acting as a substrate and is processed chemically to become hydrophilic. This processing, via adsorption of H₂SO₄, leads to a similar degree of incorporation of soluble material, independent of the source of black carbon. We plan to study combustion-generated soot particles in continuing investigations.

Using available engine emission data, we estimate the amount of SO₄ that must be oxidized in the gas phase of the plume or on the soot itself to produce these highly activated particles. Engine emission indices were taken as 0.02 g/kg fuel for soot and 1 g/kg fuel for SO₄ (Miake-Lye et al., 1992). For all the carbon particles to gain 10% by weight H₂SO₄, 0.002g H₂SO₄/kg fuel must be produced. This corresponds to oxidation of only 0.1% of the available SO₂.
The measurements of Arnold et al. (1992; 1993) suggest substantial conversion of SO₂ to H₂SO₄ in young aircraft exhaust plumes. Thus, heterogeneous formation or condensation of H₂SO₄ on a carbon core may be a significant source of active aerosols in aircraft exhaust plumes, and may compete with homogeneous nucleation in the near-field portion of the plume.

Conclusions

Spherocarb particles, activated by adsorbed H₂SO₄, were observed to hydrate under subsaturated conditions. Their hydration behavior is consistent with hydration of the adsorbed acid in the presence of the inert carbon substrate. Treated Spherocarbs appear to have soluble mass fractions and surface coverage properties similar to jet engine exhaust aerosols observed by Whitefield et al. (1993). This hydration behavior will impact the critical supersaturation and hence the ability of soot particles to act as cloud condensation nuclei. This suggests that sulfuric acid may play an important role in the activation of black carbon produced from combustion sources.

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References


