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The De-activation of Ammonium Sulfate Aerosol Particles as a function of Organic Acid Deposition onto the Particle Surface: Implications for Understanding Cloud Condensation Nuclei (CCN) Activity of Processed Ambient Aerosol Particles

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By

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Abstract:

The cloud condensation nuclei activity of organic coated ammonium sulfate particles was studied using a CCN counter in conjunction with the Aerodyne Aerosol Mass Spectrometer. The organic coatings studied were adipic acid, decanedioic acid (DEHS) and stearic acid.

It was found, that the CCN activity of ammonium sulfate particles decreased as a function of insoluble (stearic, DEHS) and slightly soluble (adipic) organic coating on the surface of the aerosol particles. Due to the liquid state of DEHS, water molecules diffused through the coating and caused a slight increase in the critical supersaturation. Water was unable to diffuse through the thick and insoluble coating of stearic acid and caused the CCN activation of the ammonium sulfate core to be suppressed within the parameters of this experiment.

1. Introduction and Theory

Atmospheric aerosol particles originate from both natural and anthropogenic sources, each of which contribute to the regional aerosol distribution. Aerosol particles can influence climate by either absorbing or reflecting incoming solar radiation as distinct bodies in the atmosphere or by serving as cloud condensation nuclei (CCN).[1] In the later case, the particle surface serves as a platform onto which water vapor will condense to form cloud droplets. In this process, the key particle properties are the chemical composition and dry particle diameter. Some atmospheric aerosol particles, such as combustion generated soot, are initially hydrophobic and therefore not active as CCN. Conversely, atmospheric salt particles such as ammonium sulfate are highly hygroscopic, which facilitates CCN activity. In the atmosphere, the chemical composition and size distribution of the aerosol particles is very complex and spatially and temporally variable. Particles undergo 'processing' as a function of atmospheric residence time, which transforms the chemical composition and size of the particle ensemble consequently influencing the CCN activity. One example of atmospheric processing is the deposition of hydrophobic material (organics) onto the surface of hydrophilic salts.

1.1 *Cloud formation and the Direct and Indirect Effects*

Clouds are formed by the lifting of humid air that cools by expansion under continuous falling pressure.[2] Relative humidity is the water-vapor content of the air relative to its content at saturation. It is also a ratio of how much energy has been used to free water from liquid to form vapor to how much energy is left. Relative humidity is expressed as a percentage and is calculated using the following equation:

$$RH = \frac{P_{(H_2O)}}{P^*_{(H_2O)}} \times 100$$ **(Eq. 1)**

RH = Relative Humidity

$P_{(H_2O)}$ is the partial pressure of water vapor in the gas mixture

$P^*_{(H_2O)}$ is the saturation vapor pressure of water at the temperature of the gas mixture.[3] (Note: All terms and symbols defined in a glossary in Section 6, Page 17)

The relative humidity increases until the air approaches saturation. If air continues cooling beyond the point of saturation, then condensation is able to occur on some of the wide variety of aerosol particles present[4]. Some of these aerosol particles are hygroscopic and promote condensation at relative humidity below 100%. But for continued

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[1] Charlson RJ, Pilat MJ (1969) Climate: The Influence of Aerosols. *Journal of Applied Meteorology*: Vol. 8, No. 6 pp. 1001–1002

[2] McGraw-Hill Encyclopedia of Science and Technology vol. 8 New York, NY McGraw-Hill Book company 2004 6th edition "Humidity " p. 547

[3] Ward, Robert De C. (1975) Note On Atmospheric Humidity In The United States. *Monthly Weather Review*: Vol. 50, No. 11 pp. 575–581

[4] Relative Humidity. In Britannica Micropedia Ready Reference; 15th Ed. Krasnogorsk, Holderness: Chicago, 2002: Vol 6, p 143.

condensation leading to the formation of cloud droplets, the air must be slightly supersaturated. Ammonium sulfate is a highly efficient cloud condensation nucleus. Condensation onto the aerosol particle continues as fast as water vapor is made available by continuous cooling of the surrounding air.[5] Cloud droplets are rarely uniform in size and can arise on nuclei of various sizes as well.

Aerosol particles tend to cause cooling of the Earth's surface directly below them. Since the majority of aerosol particles reflect sunlight back into space, they are said to have a "direct" cooling effect by reducing the amount of solar radiation that reaches the Earth's surface. The extent of this cooling effect depends on the size and chemical composition of the aerosol particles.[6]

Aerosol particles also create an "indirect" effect on climate by changing the properties of clouds. The aerosol indirect effect is currently credited with the greatest range of uncertainty amongst the known causes of radiative forcing.[7] Radiative forcing can be looked at as the change in the balance between radiation coming into the atmosphere and the radiation going out. Positive radiative forcing tends to warm the surface of the Earth, and negative forcing tends to cool the surface.[8]

In the absence of aerosol particles, there would, in effect, be no clouds in the sky. It is very difficult to form clouds without these small aerosol particles acting as "seeds" or cloud condensation nuclei (CCN) to begin the cloud formation process. With an increase in aerosol concentration, there is expected to be an increase in cloud droplet formation. [9,10] Since the total amount of condensed water in the cloud is not expected to change much, the average drop would become smaller. Smaller drops result in an increase in the reflection of sunlight. The clouds would also last longer in our atmosphere because it takes more time for small drops to coalesce into drops large enough to fall to the ground. Both effects increase the amount of sunlight that is reflected to space without reaching the surface.

During the last 30 years, scientists have identified several major aerosol types and have developed general ideas about the amount of aerosols to be found in different seasons and locations. Still, key details about the amount and properties of aerosols are needed to calculate even their current effect on surface temperatures.[11]

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[5] McGraw. Hill. Cloud Physics. In McGraw-Hill Encyclopedia of Science and Technology; 7th Ed. McGraw-Hill Professional: New York, 2002; Vol. 2, p47.
[6] Rind D, Balachandran N, Suozzo R (1992) Climate Change and the Middle Atmosphere. Part II: The Impact of Volcanic Aerosols. Journal of Climate: Vol. 5, No. 3 pp. 189–208
[7] Anderson, T. L., et al. (2003) Climate Forcing By Aerosols: A Hazy Picture. Atmospheric Science: Vol. 300, No. 5622 pp. 1103-1104.
[8] United States National Research Council (2005) *Radiative Forcing of Climate Change:* Expanding the Concept and Addressing Uncertainties, Board on Atmospheric Sciences and Climate
[9] Wise, M.E., et al. (2003). Hygroscopic growth of ammonium sulfate/dicarboxylic acids. Journal of Geophysical Research108, Article Number 4638.
[10] Abbatt, J., et al. (2005) Cloud Condensation Nucleus Activity of internally mixed ammonium sulfate/organic acid aerosol particles. Atmospheric Environment: 39, p. 4769
[11] Jones, A., et al. (1994). A Climate Model Study of Indirect Radiative Forcing by Anthropogenic Sulphate Aerosols. Nature 370: 450-53

1. 2 *Köhler Curves*

The formation of cloud droplets can be described using Köhler theory.[12] The theory assumes microscopic spherical droplets that consist of a mixture of completely dissociated electrolytic salt and water. According to the theory, the droplets are in a thermodynamic equilibrium until the saturation ratio of the water vapor reaches a certain critical value, after which the droplets are "activated" resulting in spontaneous growth into larger cloud droplets.

The "Kelvin Effect" and the "Solute Effect" are critical in understanding the Köhler Theory equations, which are in turn critical in understanding how a droplet of a certain diameter and composition responds when exposed to different supersaturations.[13] The Kelvin Effect thermodynamically explains the change in equilibrium vapor pressure over the curved surface of a droplet. The Solute effect explains the change in vapor pressure of a solution in terms of the mole fraction of solute.

1.2a *The Kelvin Equations*

The curved characteristic of an atmospheric water drop thermodynamically differentiates the drop from a flat surface of water.[14]

$$\Delta G = G_{droplet} - G_{purevapor} \qquad \textbf{(Eq. 2)}$$

Equation 2 calculates the change of the Gibbs energy and can pertain to the formation of a particle droplet of radius R_p containing n molecules.

The total number of initial vapor molecules is assumed to be N_T. When a drop forms, the remaining number of vapor molecules is $N_1 = N_T - n$. If we take g_v and g_l as the Gibbs free energies of a molecule in both the vapor and liquid phases, respectively, we obtain the equation:

$$\Delta G = N_1 g_v + n g_l + 4\pi R_p^2 \sigma - N_T g_v \qquad \textbf{(Eq. 3)}$$

Where $4\pi R_p^2 \sigma$ is the free energy of the droplet related with radius of curvature R_p and a surface tension, σ. This can be rewritten as:

$$\Delta G = n(g_l - g_v) + 4\pi R_p^2 \sigma \qquad \textbf{(Eq. 4)}$$

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[12] Seinfeld J.H., Pandis, S.N. (1998) Atmospheric Chemistry and Physics: From Air Pollution to Climate Change. Wiley Interscience, US. Ed. 2nd. pp. 787-792.

[13] Kumar, P. et al. Organic Acids as Cloud Condensation Nuclei: Laboratory Studies of Highly Soluble and Insoluble Species. (2003) Atmospheric Chemistry and Physics Discussions.3, pp 949-982.

[14] Nenes, A. (2001) Kinetic Limitations on Cloud Droplet Formation and Impact on Cloud Albedo. Tellus B, 3. pp 133-149.

The number of molecules in the drop, n, and the drop radius R_p are related by

$$n = \frac{4\pi R_p^3}{3v_l} \qquad \text{(Eq. 5)}$$

where v_l is the volume of a liquid phase molecule. The change in Gibbs Free energy is now:

$$\Delta G = \frac{4\pi R_p^3}{3v_l}(g_l - g_v) + 4\pi R_p^2 \sigma \qquad \text{(Eq. 6)}$$

To find the difference in the Gibbs Free energy per molecule of the liquid and vapor states, $g_l - g_v$, it is necessary to maintain a constant temperature. This results in $dn_i = 0$, $dg = vdp$ as well as $dg = (v_l - d_v)dp$. Since $V_v \gg v_l$ for conditions of interest, we are able to overlook v_l relative to v_v in this equation. In turn, $dg = -v_v dp$. Since the vapor phase is assumed to be ideal, $v_v = kT/p$. Resulting in the integral, [15]

$$g_l - g_v = -kT \int_{p_w^\circ}^{p_w} \frac{dp}{p} \qquad \text{(Eq. 7)}$$

Where p_w° is the vapor pressure over a flat surface and p_w is the actual equilibrium partial pressure over the liquid.[16] The equation can be rewritten as:

$$g_l - g_v = -kT \ln \frac{p_w}{P_w^\circ} \qquad \text{(Eq. 8)}$$

and the ratio p_w / p_w° is then defined as the saturation ratio S. The change in Gibbs free energy is now expressed as[17]:

$$\Delta G = -\frac{4}{3}\pi R_p^3 \frac{kT}{v_l} \ln S + 4\pi R_p^2 \sigma \qquad \text{(Eq. 9)}$$

It is necessary to note that when $S < 1$, both terms in the previous equation are positive and ΔG increases with R_p. A change in G that is greater than 0, means that condensation is thermodynamically unfavorable. On the other hand, when $S > 1$, ΔG contains both positive and negative contributions. At small values of R_p the surface tension term dominates and the behavior of the ΔG is similar to the $S < 1$ case. If R_p increases, the first term on the right-hand side of **Eq. 9** becomes more important, resulting in a ΔG that reaches a maximum value ΔG^* at $R_p = R_p^*$ and then goes on to decrease. Thus, there is a critial droplet size above which further growth is favorable and below which is unfavorable. The radius corresponding to the maximum can be calculated by setting $\partial \Delta G / \partial R_p = 0$ to get:

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[15] Seinfeld, Pandis (1998) p. 520
[16] Seinfeld, Pandis (1998) p. 520
[17] Seinfeld, Pandis (1998) p. 522

$$R_p^* = \frac{2\sigma v_l}{kT \ln S} \text{S}$$ **(Eq.10)**

Since ΔG is a maximum at $R_p = R_p^*$, the equilibrium at this point is metastable. The equilibrium radius of a pure droplet is related to the physical properties of the substance, σ and v_l, and to the saturation ratio S of its environment. Using the saturation ratio, the Kelvin equation cab be rewritten as:

$$p_w = p_w^\circ \exp\left(\frac{2\sigma M}{RT\rho_l R_p}\right)$$ **(Eq.11)**

where M is the molecular weight of the substance and ρ_l is the liquid phase density.[18]

1.2b *Raoult's Law:*

The second necessary part of understanding the Köhler Curve involves the vapor pressure of each chemical component being dependent on the vapor pressure of the individual components and the mole fractions of the component present in the solution[19]

When the components in the solution have reached chemical equilibrium, the total vapor pressure of the solution is:

$$P_{solution} = \left(P_1\right)_{pure} X_1 + \left(P_2\right)_{pure} X_2 \ldots$$ **(Eq.12)**

Where $\left(P_i\right)_{pure_i}$ is the vapor pressure of the pure component and X_i is the mole fraction of that component in the water. As the number of components increases, individual vapor pressures decrease since the mole fractions of all components decrease. Thus, if a pure solute with no vapor pressure is dissolved in water, the vapor pressure of the water/solute solution will be lower than that of the pure water.

This law is exactly correct only under the assumption that the chemical interactions between water and solute molecules or ions are equal to the interactions between water molecules. This makes it difficult to compare actual measured vapor pressures to the theoretical values calculated from Raoult's law.

If the measured vapor pressure value is less than the calculated value, fewer molecules have left the solution than expected. The strength of interaction between the liquids may be greater than the intermolecular bonding within the individual liquids, so fewer molecules have enough energy to leave the solution. Conversely, if the vapor pressure is greater than the predicted value more molecules have left the solution than

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[18] Seinfeld, Pandis (1998) p. 523
[19] McGraw, Hill. Vapor Pressure.

expected, due to the interaction between the solute and solvent (water) being less strong than the interaction within each pure substance.[20]

1.2c *Köhler Equations:*

The description of the equilibrium size of a droplet corresponding to a specific water saturation ratio was founded by Köhler in 1936[21]. The Köhler Theory can be conceived as the competition between the previous two expressions of the properties that determine the activation of particles: the curvature term (Kelvin) and the solute term. (Raoult)

The equilibrium vapor pressure, p_ω, over a spherical solution droplet, at a particular temperature T, is expressed with the following equation:

$$\frac{p_\omega}{p^0(T)} = S = a_\omega \exp\left(\frac{4\sigma_{sol}\overline{V_\omega}}{RTD_p}\right) = \frac{RH}{100} \qquad \textbf{(Eq.13)}$$

In this equation, a_ω is the water activity of the solution droplet, σ_{sol} is the surface tension of the solution, $\overline{V_\omega}$ is the partial molar volume of water in solution, R is the universal gas constant, and D_p is the droplet diameter. The partial molar volume, water activity and surface are all functions of composition and temperature. If the droplet is in equilibrium with its environment, the saturation ratio can be assimilated to the fractional ambient relative humidity, $RH/100$.

The basis of the Köhler Theory is formed by Eq. 13.[22] It is the basis of our hypothetical understanding of CCN activity for ammonium sulfate by theoretically predicting the CCN activity of aerosols in terms of critical supersaturations.[23] When the saturation ratio, S is plotted against D_p for a particular mass of solute there is a maximum. The saturation ratio at this maximum becomes the critical supersaturation S_c. In general when particles grow past this diameter associated with S_c they are considered cloud droplets. The partial molar volume of water in solution can be simplified to:

$$\overline{V_\omega} = \frac{MW_\omega}{\rho_{sol}}\left(1 + \frac{X}{\rho_{sol}} \cdot \frac{d\rho_{sol}}{dX}\right) \qquad \textbf{(Eq.14)}$$

And can also be formulated by the following[24]:

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[20] Seinfeld and Pandis (1998) pp. 787-788
[21] Sun, J., Ariya, P.A. (2006) Atmospheric organic and bio-aerosols as cloud condensation nuclei (CCN): A review. Atmospheric Environment, Volume 40, Issue 5. pp 795-820.
[22] Sun, J, Ariya, P.A.(2006)
[23] Giebl, H. et al. (2002) CCN activation of oxalic and malonic acid test aerosols with the University of Vienna cloud condensation nuclei counter. Journal of Aerosol Science, Volume 33, Issue 12; pp 1623-1634.
[24] Seinfeld and Pandis (1998)

$$\ln\left(\frac{p_\omega}{p^o}\right) = \frac{A}{D_p} - \frac{B}{D_p^3} \quad \text{where,} \tag{Eq.15}$$

$$A = \frac{4MW_w\sigma_w}{RT} \cong \frac{0.66}{T} \tag{Eq.16}$$

$$B = \frac{6n_s M_w}{\pi_{\rho w}} \cong \frac{3.44\times10^{14}\,vM_s}{MW_s} \tag{Eq.17}$$

Where the units of A and D_p are microns (μm), and B are cubic microns (μm^3).

These equations express the two effects that determine the vapor pressure over an aqueous solution droplet. For a pure water drop there is no solute effect and the Kelvin effect results in higher vapor pressures over the curved surface of a water droplet compared to a flat surface. By contrast, the vapor pressure of an aqueous solution drop can be larger or smaller than the vapor pressure over a pure water surface depending on the magnitude of the solute effect term, B/D_p^3, relative to the curvature term, A/D_p. Both effects increase with decreasing droplet size, but the solute effect increases much faster.[25]

A/D_p (Kelvin Equation) and the B/D_p^3 (Solute Effect) make up the Theoretical Köhler Curves used in the experiment.
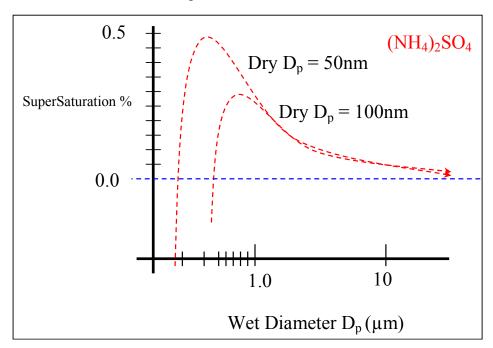

Figure 1: Kohler Curves for NaCl and $(NH_4)_2SO_4$ particles with dry diameters of 50 and 100 nm at room temperature.

[25] Brechtel, F. J., Kreidenweis, S. M. (2000) Predicting particle critical supersaturation from hygroscopic growth measurements in the humidified TDMA. Part II: Laboratory and ambient Studies. Journal of Atmospheric Science: Vol 57 pp 1872-1887.

All curves similar to **Figure 1** pass through a maximum at the critical droplet diameter D_{pc},

$$D_{pc} = \left(\frac{3B}{A}\right)^{1/2} \qquad \textbf{(Eq.18)}$$

The saturation relative to a flat pure water surface required for droplet equilibrium is expressed as $\dfrac{p_w}{p_w^\circ}$ and at the critical diameter, the critical saturation S_c is:

$$\ln S_c = \left(\frac{4A^3}{27B}\right)^{1/2} \qquad \textbf{(Eq.19)}$$

The Raoult Effect represents the portion of the Köhler curve where the graph curves upward as a function of the increasing D_p. As the droplet diameter increases, the comparative importance of the Kelvin effect over the solute effect also increases. When the droplet increases beyond the critical diameter, the Kelvin effect is apparent.[26] All Köhler curves approach the Kelvin equation, represented by pure water droplet equilibrium. [27]

The critical super saturation S_c is an important property. If the environment has reached a saturation larger than S_c the particle is said to be activated and starts growing rapidly, becoming a cloud droplet. For spherical aerosol particles of a diameter d_s, density ρ_s and the molecular weight M_s, the number of moles in the particle is given by:

$$n_s = \frac{v\pi d_s^3 \rho_s}{6M_s} \quad \text{which then gives us } \ln S_c = \left(\frac{4A^3 \rho_w M_s}{27 v \rho_s M_w d_s^3}\right)^{1/2} \qquad \textbf{(Eq.20)}$$

This equations gives the critical saturation for a dry particle of diameter d_s. When a fixed saturation S exists, all particles whose critical saturation S_c, exceeds S come to a stable equilibrium size at the appropriate point on the Köhler Curve for their species. All particles whose S_c is below S become activated and grow as long as $S > S_c$.[28]

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[26] Sjogren, S., Gysel, M., et al. (2007) Hygroscopic growth and water uptake kinetics of two-phase aerosol particles consisting of ammonium sulfate, adipic and humic acid mixtures. Journal of Aerosol Science, Vol 38, No. 2 pp 157-171.
[27] Cruz, Pandis. (1997)
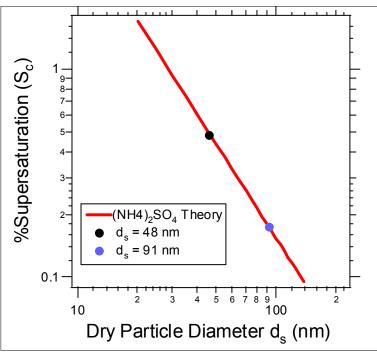[28] Seinfeld, Pandis (1998) p. 782

Figure 2: Critical supersaturation for activating aerosol particles composed of $(NH_4)_2SO_4$ as a function of dry particle diameters at room temperature.

Along with an increasing value of supersaturation below the critical supersaturation S_c comes a unique equilibrium droplet size. Once the droplet grows beyond its critical size (as S increases above S_c) the droplet will exhibit unhindered growth unless S is reduced below the equilibrium value of S at the instantaneous value of r.

1.3 *Relationship of Köhler Theory to Laboratory Experiment:*

The subject of this experiment is the transformation of originally hydrophilic ammonium sulfate aerosol particles to hydrophobic compounds using organic compounds. Ammonium sulfate aerosols affect climate by direct radiative effects. Sulfate is an important contributor to global warming because of its chemical properties. This type of CCN limits precipitation, the principal process by which aerosols are removed from the atmosphere. The activation of ammonium sulfate aerosol particles inevitably increases aerosol lifetime and concentration.

Due to time and atmospheric processing, coatings such as organics, have the ability to change both the size and surface chemical composition of the original ammonium sulfate particles. This atmospheric processing may result in a hydrophobic particle and affect the hygroscopicity that is necessary to address the ammonium sulfate particles' role as cloud condensation nuclei.

Using the experimental setup shown in **Figure 3**, ammonium sulfate aerosols were generated using an aspirator and ammonium sulfate/water solution. These particles were then dried and size-selected using a Differential Mobility Analyzer (DMA) and subsequently mixed with controlled amounts of vapor of specific organic compounds.

The amount of these coated particles per cubic centimeter of air was determined by a Condensation Particle Counter (CPC) and then the flow was sampled into an Aerosol Mass Spectrometer (AMS) to understand the composition and size of the particles. The aerosol flow also travels through a Cloud Condensation Nuclei Counter (CCN) to compare the size and composition of these particles found from the AMS, with the CCN activating capability of our generated aerosol particles.
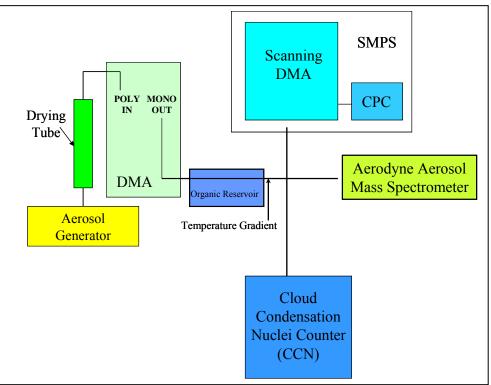
2. Experimental Details

Figure 3: Diagram of the experimental apparatus, showing the path the ammonium sulfate aerosol particles travel after being created by the aerosol generator.

The instruments used throughout this experiment were required to obtain accurate and meaningful data. Ammonium sulfate aerosol particles were obtained using an aerosol generator. The aerosol generator uses compressed nitrogen which expands through an orifice to form a high-velocity jet. The ammonium sulfate solution is then aspirated into the generating section through a vertical passage and is made into aerosol particles by the jet. Large droplets are removed by impaction on the wall opposite the jet and the excess solution is drained at the bottom of the generator back into the solution container. The ammonium sulfate aerosol particles leave the generator through the top.

Once created, the aerosol particles pass through a drying tube. The drying tube uses calcium sulfate to absorb the excess water from the wet ammonium sulfate aerosol particles. This takes place using the following processes:

$$(NH_4)_2SO_4 \cdot H_2O \ (aq) \rightarrow (NH_4)_2SO_4 + H_2O \ (g)$$

$$H_2O \text{ (g) diffuses to the } CaSO_4 \text{ via:}$$
$$CaSO_4 + Air (H_2O \text{ (g)}) \rightarrow CaSO_4 \cdot H_2O$$

The polydisperse distribution of ammonium sulfate particles, characterized as particles of varied sizes, [29] leaves the drying tube free of water and travels on to the Differential Mobility Analyzer (DMA). The DMA separates particles based on their electrical mobility. When the polydisperse ammonium sulfate aerosol particles pass through a Krypton 85 charger, an equilibrium charge level on the particles is established. Particles receive either a positive, negative, or zero charge. By using an electric field created within the column by setting a certain voltage, the particles are separated according to their electrical mobility. This parameter is inversely related to particle size and proportional to the number of charges on the particles. Transmission of particles of a certain size depends upon the relationship between the flow fields, electric field, particle size and particle charge. The result is that we can tune the device to select out one particular size of aerosol particles, a "monodisperse" distribution, from 10 to 1000 nm.

Real time concentrations of the ammonium sulfate aerosol particles were found using a Condensation Particle Counter (CPC). The CPC works on light scattering principles. The CPC utilizes a laser diode to illuminate the particles. This laser shines through an optical block that holds mirrors and photo detectors. The aerosol particles are drawn through the laser beam by a vacuum pump. As the entrained particles pass through the laser beam, the laser light interacts with particles and light is scattered. As the light scatters, it is picked up by the mirrors. These mirrors then focus the scattered light onto the photo-detector which converts the light energy from each particle into a pulse of electrical energy. The height of the signal is measured and referenced to a calibration curve (generated using polystyrene latex particles of known size). This determines the size of the particles. By counting the number of pulses, the quantity can also be determined.

The concentration of aerosol particles is vital to our Cloud Condensation Nuclei Counter. Once the stream of particles is sampled by the CPC and the concentration is known, the concentration of CCN-activating particles is then determined. The device measures the number concentration of particles upon which water vapor condenses at high values of supersaturation, relative to equilibrium vapor pressure over the liquid phase of the substance.

To measure CCN activity, aerosols must be subjected to a supersaturated environment, which is commonly done with a thermal diffusion chamber. Two wetted plates, separated by a small distance, are held at different temperatures. Because of the nonlinear dependence of the saturation vapor pressure on temperature, the air between the two plates is slightly supersaturated. The degree of supersaturation can be calculated if the distance between the two plates and both temperatures are known.

The ammonium sulfate aerosol particles, which have a theoretical critical supersaturation S_c,[30] are subjected to supersaturations both below and above S_c to obtain a complete range of activation. The particles are monitored by an optical particle counter that records the number of aerosol particles that become CCN at the different supersaturations. The ratio of the total number of activated particles to total number of

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[29] Seinfeld, Pandis. (1998) p. 97
[30] Seinfeld, Pandis. (1998) pp. 510-517

particles measures the relative activation at a specific supersaturation. The supersaturation is constant within the column and can be varied between 0.07% - 2% by changing the temperature gradient.

The chemical composition of our coated aerosol particles is determined by the Aerodyne Aerosol Mass Spectrometer. The Aerodyne AMS provides real-time size resolved composition analysis of volatile and semi-volatile aerosol particles.[31] The aerosol particles enter the Aerodyne AMS through a particle-sampling inlet that restricts the flow with a 100 μm orifice. The particles then travel through a lens that focuses the aerosols into a tight beam of approximately one millimeter in diameter. The aerosols exit the lens and are accelerated in a supersonic expansion caused by the difference in pressure between the aerosol-sampling chamber and the aerodynamic particle-sizing chambers. Here, different sized particles attain different velocities.

After passing through the focusing lens, the aerosol particles enter the particle-sizing chamber. This chamber contains a rotating chopper wheel with two radial slits located 180° apart that intercepts the focused particle beam. The chopper is able to be placed so it can either (a) completely block the beam so no particles pass through, (b) not block the beam so that all particles pass through, or (c) at a chopping position that allows particles to pass through the slits only. The time of flight (TOF) between the chopper and the detector is a measurement of a particle's velocity; from this measurement the particle's aerodynamic diameter (D_{aero}) can be determined.

The particles that pass through the flight chamber are directed onto a heated surface. When the aerosol particles collide with this heated surface, non-refractory particles flash vaporize under high-vacuum conditions. The vaporization process occurs directly inside an electron impact ionizer where the vaporized constituents are converted to positive ions, which can then be detected by the mass spectrometer.

3. Results & Discussion:

3.1 Uncoated Ammonium Sulfate Aerosol Particles

Due to the highly soluble nature of ammonium sulfate, the CCN activity curves show that the aerosol particles readily absorb water and form cloud droplets. From these spectra, we can obtain the critical supersaturation, when 50% of the particles become activated. This number is then plotted against the dry diameter of the mixed ammonium sulfate particle and compared with the theoretical Critical Supersaturations for ammonium sulfate calculated by the Köhler Equation. It was found that the Critical Supersaturations of the ammonium sulfate particles fell directly upon the theoretical line for various dry diameters. (**See figures 4 & 5**)

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[31] Department of Chemistry (Analytical, Environmental, and Atmospheric Chemistry Division). Dept. home page. Spring 2007. University of Colorodo, Boulder. 12 Apr. 2007 <http://cires.colorado.edu/jimenez/>.
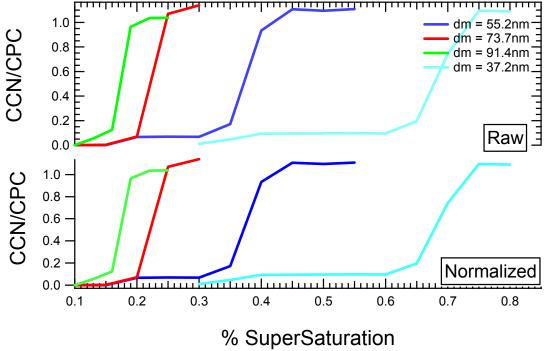
Figure 4: Cloud Condensation Nuclei curves of pure ammonium sulfate at different particle diameters. Due to fluctuations in CPC readings, the raw data was normalized to 100% at full activation in order to correct instrumental errors.

dry diameter (nm)	S_c of 37 nm AS Core + DEHS	dry diameter (nm)	S_c of 37 nm AS core + SA	dry diameter (nm)	S_c 38 nm AS core + Adipic
37	0.65	37	0.74	38.5	0.7
48	0.64	68	0.745	51	0.6
113	0.44	88	0.921	61	0.52
157	0.44	118	—	71	0.5
209	0.488	157	—	85	0.34
				118	0.21
	S_c of 78 nm AS Core + DEHS		S_c of 55 nm AS core + SA		S_c 57 nm SA core + Adipic
76	0.21	55	0.36	57	0.34
79	0.2	74	0.399	63	0.335
91	0.18	85	0.399	71	0.32
113	0.164	98	0.54	88	0.27
157	0.145	122	0.98	113	0.19
188	0.14				
			S_c of 76 nm AS core + SA		
		78	0.21		
		98	0.21		
		113	0.29		
		126	0.838		
		168	0.912		

Table 1: Table of dry diameters and corresponding S_c for the experimental mixed sulfate/organic aerosol particles.
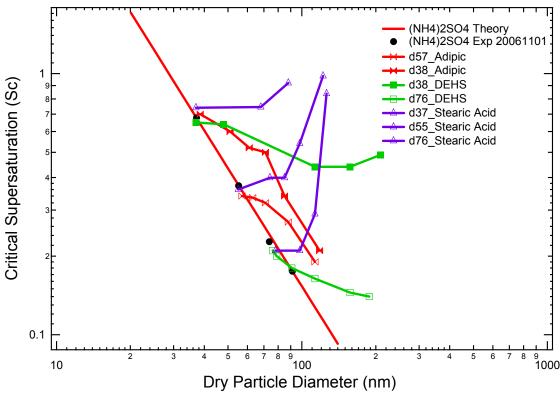
Figure 5: S_c vs. D_d plot for all three mixed sulfate/organic particles showing deviations from theoretical ammonium sulfate and experimental ammonium sulfate (black). (See appendix for individual plots)

3.2 Ammonium Sulfate Aerosol Particles Coated with Organic Substances

As the sulfate cores are coated with organics of varying solubilities, the CCN activity decreases, and thus the Critical Supersaturation changes as well. The new coated particles have larger dry diameters and are compared with ammonium sulfate particles of similar size. As the ammonium sulfate aerosol particles grow in size, they activate at lower Supersaturations. However, when the S_c of mixed aerosol particles are determined and plotted against their dry diameter, they no longer fall in line with the theoretical ammonium sulfate. As the chemical composition changes, so to does the S_c for a specified dry diameter. The three organics used, adipic, DEHS and stearic acid, all deviated from the theoretical line independently of one another. Each organic showed its own valid trend.

Secondary organic aerosol material is formed in the atmosphere by the mass transfer to the aerosol phase of low vapor pressure products of the oxidation of organic gases. As organic gases are oxidized in the gas phase, their oxidation products accumulate. Experimentally, the organic vapors have low to zero solubility and condense on the available ammonium sulfate particles in an effort to establish equilibrium between the gas and aerosol phases. The thermodynamic principles discussed in the introduction can be used to explain the partitioning of organic compounds between gas and aerosol phases.

For high organic aerosol loadings, or very low vapor pressures and a high temperature reservoir, virtually all organic vapor will condense onto the aerosol phase. Ammonium Sulfate aerosol particles are able to adsorb oxygenated organic vapor

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molecules onto their surfaces. The interactions between the adsorbed molecules and the ammonium sulfate particle surface are complex and, simply put, involve both physical and chemical forces.

The adsorption process first involves the partial covering of the particle surface with organic vapor molecules, eventually forming a monolayer. Depending on the temperature of the reservoir, additional layers are added, and therefore the coating thickness increases. The monolayer interacts with the particle surface, and the succeeding layers interact primarily with the already adsorbed molecules. If the organic molecules are slightly soluble (such as the adipic acid), water is still able to permeate the coating. However, the surface area of the ammonium sulfate is very much limited and the Sc of the mixed particle does decrease as a function of the organic adipic acid coating.

The organics used in this experiment are representative of existing organic compounds prevalent in the atmosphere.

3.3. Adipic Acid

Adipic Acid is a white crystalline powder and is only slightly soluble (1.4 g/100ml H_2O at 15°C) in water. When ammonium sulfate aerosol particles are coated in this organic, they avert to the right of the theoretical ammonium sulfate line and then proceed to become parallel. Adipic acid has poor solute solubility and surface hydrophobicity.[32]

Products like adipic acid also have low vapor pressures. Supersaturations of these organic gases, as in the coating reservoir, create an excess and condense onto any of the available aerosol particles, leading to the production of an organic aerosol coating. If the gas-phase concentration of adipic acid is reduced to less than the saturation value as a result of dilution or the deposition, the aerosol species evaporates in an effort to maintain thermodynamic equilibrium.[33]

According to the above description of secondary organic aerosol formation, adipic acid should be transferred to the aerosol phase if its gas-phase mixing ratio exceeds the saturation mixing ratio of pure adipic acid. The mixing ratio is the ratio of the mass of a variable atmospheric constituent to the mass of dry air.

It is reasonable that a small core of ammonium sulfate covered entirely by adipic acid retains a low CCN activating ability, but still maintains consistent activation to the right of the theoretical line. Since Adipic Acid deliquesces at 99.9% relative humidity,[34] it is possible that there is little water uptake connected with the adipic acid layer when the dry diameters increase. Instead, the activation is a result of the diffusion of water through the adipic acid onto the ammonium sulfate core. If any part of the ammonium sulfate core is exposed, water will adsorb onto the surface to form a cloud droplet. (**see Figures 6, 7, 8** for detailed CCN spectra and deviations from theoretical ammonium sulfate)

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[32]Cruz & Pandis, (1997) ; Corrigan & Novakov, 1999; Prenni et al., 2001

[33] Pilinis, C., Seinfeld, JH. (1988) Development and evaluation of an eulerian photochemical gas aerosol model. Atmospheric Environment. Vol. 22, No. 9

[34] Marcolli, C.,(200) Water activity in polyol/water systems: new UNIFAC Parameterization Atmospheric Chemistry and Physics. Vol 5. pp 1545-1555

3.4. DEHS

Decanedioic acid (DEHS) is a colorless liquid and is insoluble in water. When the ammonium sulfate particles were coated with DEHS, the S_c of the mixed Sulfate/DEHS particles only slightly decreased with an increase in dry diameter and differed very little from those of the core sulfate particle. The increase in particle size had little effect on the S_c. If the ammonium sulfate core was completely covered with DEHS, there should theoretically be no CCN activity due to its insolubility. For high relative humidities, secondary organic aerosol compounds may exist in three phases, gas, organic aerosol material and aqueous.[35] Because DEHS is insoluble, it cannot exist as an aqueous solution, nor can it react with water. However, due to its liquid state, water molecules may be able to more easily and quickly penetrate the organic coating and react with the ammonium sulfate core. Thus, a water droplet is able to form no matter the coating thickness and the S_c would have a practically unchanged Sc. (**see Figures 9, 10, & 11** for detailed CCN spectra and deviations from theoretical S_c)

3.5. Stearic Acid

Stearic acid is a completely insoluble solid. When the ammonium sulfate particles were coated with stearic acid, the S_c increased as the coating thickness of stearic acid increased. The thinner coats of the stearic acid did not change the S_c as dramatically as did the thick coats, but there is no doubt that it took a greater S_c to activate the CCN into droplets. With thicker coats, it took a high S_c level for the mixed AS/Stearic Acid particles to become CCN activating. It seemed as though the particles were heading for complete deactivation due to no diffusion through the solid stearic acid coat.

Thin coats of stearic acid also decrease the degree of activation, but not as readily as the thicker coats. Ammonium sulfate may be exposed to the gaseous surroundings and thus able to deliquesce. An exaggerated divergent behavior from the theoretical ammonium sulfate graph is observed, especially at larger particle diameters with greater coating thicknesses. The hygroscopic properties of the underlying ammonium sulfate particle may be completely deactivated due to a thick uniform coat of a solid insoluble organic like stearic acid. (**see Figures 12, 13, 14 & 15** for detailed CCN spectra and deviations from theoretical ammonium sulfate)

4. Conclusion

The CCN activity of ammonium sulfate particles decreases due to the adsorption of insoluble and slightly soluble organic material onto the surface of the aerosol particles. Due to the liquid state of DEHS, water molecules more easily diffuse through the coating and come into contact with the soluble ammonium sulfate core causing a slight increase in the critical supersaturation.

A substantial coating of a solid organic, such as stearic acid, seems to have the ability to fully suppress the hygroscopic, CCN activating ability of ammonium sulfate due to the inability of water to diffuse through the thick insoluble, coating. On the other hand, a solid coating of adipic acid changed the hygroscopicity of the ammonium sulfate core, but does not suppress the CCN activating ability altogether.

The deactivation trends of the mixed ammonium sulfate and organic particles, confirms the assumption that highly soluble ammonium sulfate is capable of having

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[35] Pandis and Seinfeld (1998) pp. 745-750

properties similar to those of the organic coatings. The effect of the solutes on the vapor-pressure-lowering seems to be cumulative.

6. Appendix

Cloud Condensation Nuclei (CCN): Small particles about which cloud droplets coalesce.[36]

ΔG : Change in Gibbs Free Energy

$P_{(H_2O)}$: Partial pressure of water vapor in the gas mixture

$P^*_{(H_2O)}$: Saturation vapor pressure of water at the temperature of the gas mixture.

N_T : Total number of initial vapor molecules.

g_v : Gibbs free energy of a molecule in vapor phase

g_l : Gibbs free energy of a molecule in liquid phase.

R_p : Radius of curvature

σ : Surface tension

n : Number of molecules in the droplet

v_l : Volume of a liquid phase molecule

p_w° : Vapor pressure, A, over a flat surface

p_w : Equilibrium vapor pressure over water

p_w / p_w° = Saturation ratio relative to a pure flat water surface

M : Molecular weight of a substance

ρ_l : Liquid phase density

$P_i = X(P_i)_{pure\,i}$: Individual vapor pressure for each component

$(P_i)_{pure\,i}$: Vapor pressure of the pure component

X_i : Mole fraction of the component in solution.

p_ω : Equilibrium Vapor pressure over a spherical solution droplet

a_ω : Water activity of a solution droplet

$\overline{V_\omega}$: Partial molar volume of water in solution

R : Universal gas constant

D_p : Droplet diameter (nm)

S : Supersaturation

S_c : Critical supersaturation

D_{pc} : Critical droplet diameter

d_s : Diameter of spherical aerosol particles

ρ_s : Density of spherical aerosol particles

polydisperse: Characterized by particles of varied sizes in a dispersed system[37]

Monodisperse: Characterized by particles of uniform size in a dispersed phase[38]

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[36] R. Charlson, James Lovelock, M. Andreae and S. Warren (1987). Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. Nature, 326, 655-661.
[37] Merriam-Webster Online Dictionary copyright © 2005 by Merriam-Webster, Incorporated
[38] Merriam-Webster Online Dictionary copyright © 2005 by Merriam-Webster, Incorporated
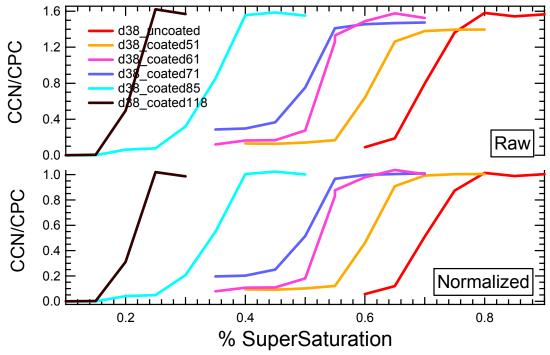
Figure 6: Cloud Condensation Nuclei curves of 38 nm Ammonium Sulfate cores coated with Adipic Acid
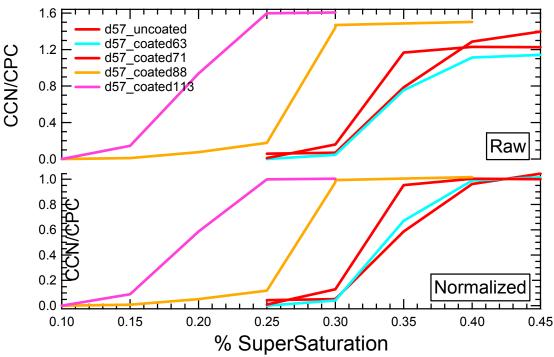

Figure 7: Cloud Condensation Nuclei curves of 57 nm Ammonium Sulfate cores coated with Adipic Acid
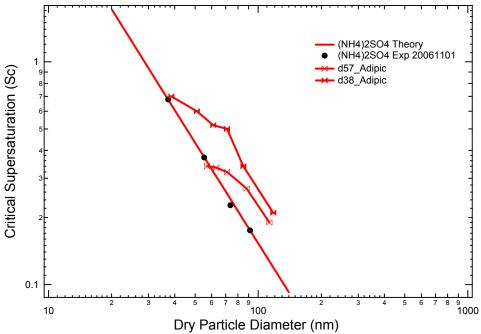
Figure 8: S_c vs. D_d plot for ammonium sulfate cores coated with adipic acid showing the deviation trend from the theoretical ammonium sulfate.
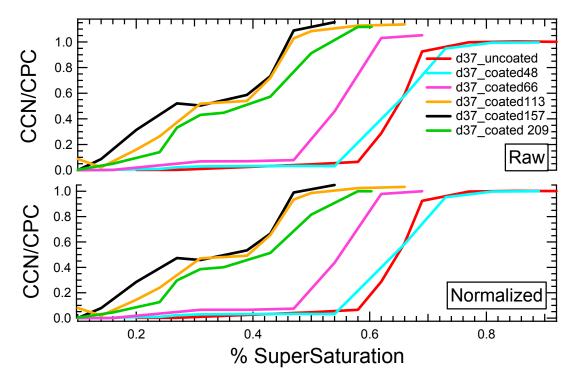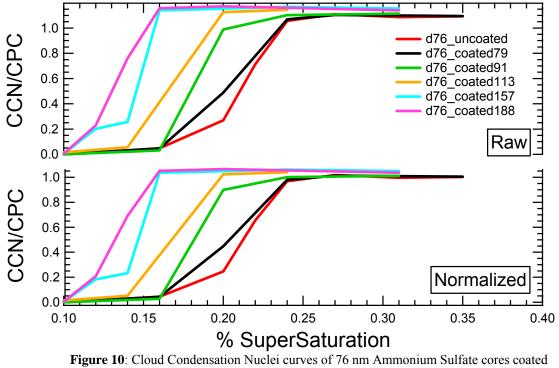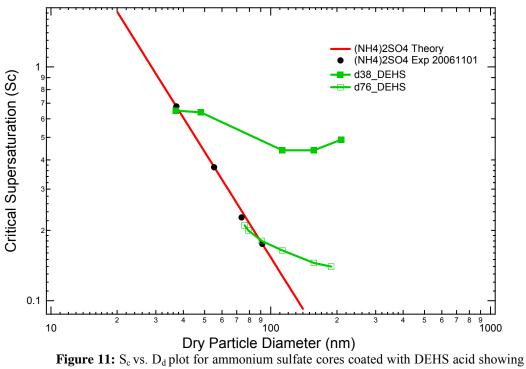

Figure 9: Cloud Condensation Nuclei curves of 37 nm Ammonium Sulfate cores coated with DEHS

Figure 10: Cloud Condensation Nuclei curves of 76 nm Ammonium Sulfate cores coated with DEHS

Figure 11: S_c vs. D_d plot for ammonium sulfate cores coated with DEHS acid showing the deviation trend from the theoretical ammonium sulfate.
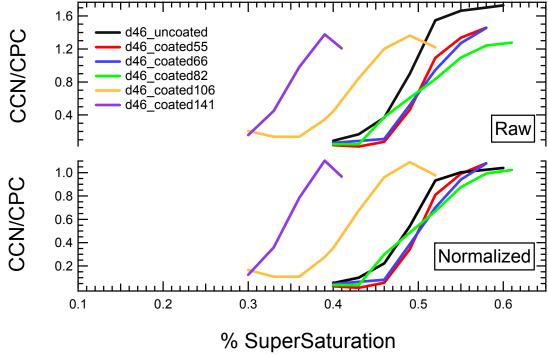
Figure 12: Cloud Condensation Nuclei curves of 46 nm Ammonium Sulfate cores coated with Stearic Acid
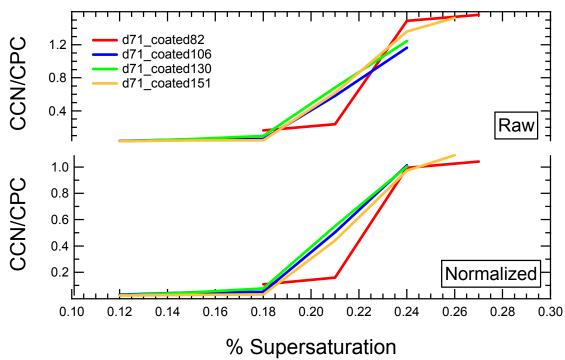

Figure 13: Cloud Condensation Nuclei curves of 71 nm Ammonium Sulfate cores coated with Stearic Acid
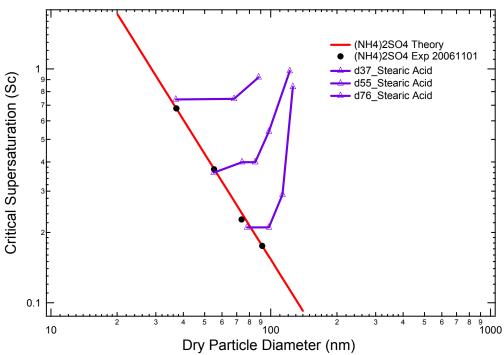
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Figure 14: S_c vs. D_d plot for ammonium sulfate cores coated with Stearic acid showing the deviation trend from the theoretical ammonium sulfate.

7. References

Abbatt, John; Broekhuizen, K.; Kumar, Pradeep. (2005) Cloud Condensation Nucleus Activity of internally mixed ammonium sulfate/organic acid aerosol particles. Atmospheric Environment: 39, pp. 4767–4778

Anderson, Theodore L.; Charlson, Robert J.; Schwartz, Stephen E.; Knutti, R.; Boucher, O.; Rodhe, H.; Heintzenberg, Jost. (2003) Climate Forcing By Aerosols: A Hazy Picture. Atmospheric Science: Vol. 300, No. 5622 pp. 1103-1104.

Charlson RJ..; Pilat M.J. (1969) Climate: The Influence of Aerosols. Journal of Applied Meteorology: Vol. 8, No. 6 pp. 1001–1002

Cruz, C.N.; Pandis, S.N. (1997) A study of the ability of pure secondary organic aerosol to act as cloud condensation nuclei. Atmospheric Environment 31, pp 2205–2214.

Cruz, C.N.; Pandis, S.N., (1998) The effect of organic coatings on the cloud condensation nuclei activation of inorganic atmospheric aerosol. Journal of Geophysical Research 103, pp. 13111–13123.

Cruz, C.N.; Pandis, S.N., (2000.) Deliquescence and hygroscopic growth of mixed inorganic–organic atmospheric aerosol. Environmental Science and Technology 34, pp. 4313–4319.

Jones, A. ; Roberts D. L.; Slingo, A. (1994). A Climate Model Study of Indirect Radiative Forcing by Anthropogenic Sulphate Aerosols. Nature 370: 450-53

Kumar, P.; Broekhuizen, K.; Abbatt, J. P. D. Organic Acids as Cloud Condensation Nuclei: Laboratory Studies of Highly Soluble and Insoluble Species. (2003) Atmospheric Chemistry and Physics Discussions.3, pp 949-982.

McGraw Hill. Humidity. In McGraw-Hill Encyclopedia of Science and Technology; 7th Ed. McGraw-Hill Professional: New York, 2002; Vol. 8, p547.

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Nenes, Athanasios; Ghan, S.; Hayder, A.; Chuang, P.Y.; Seinfeld, J.H. (2001) Kinetic Limitations on Cloud Droplet Formation and Impact on Cloud Albedo. Tellus B, 3. pp 133-149.

Pandis, Spyros N.; Seinfeld, John H. Atmospheric Chemistry and Physics: From Air Pollution to Climate Change. Wiley Interscience, US. Ed. 2nd.

Relative Humidity. In Britannica Micropedia Ready Reference; 15th Ed. Krasnogorsk, Holderness: Chicago, 2002: Vol 6, p 143.

Rind D.; Balachandran N.; Suozzo, R. (1992) Climate Change and the Middle Atmosphere. Part II: The Impact of Volcanic Aerosols. Journal of Climate: Vol. 5, No. 3 pp. 189–208

United States National Research Council (2005) Radiative Forcing of Climate Change: Expanding the Concept and Addressing Uncertainties, Board on Atmospheric Sciences and Climate

Ward, Robert C. Note On Atmospheric Humidity In The United States. Monthly Weather Review: Vol. 50, No. 11 pp. 575–581

Wise, M.E.; Surratt, J.D.; Curtis, D.B.; Shilling, J.E.; Tolbert, M.A.(2003). Hygroscopic growth of ammonium sulfate/dicarboxylic acids. Journal of Geophysical Research 108, Article Number 4638.