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HETEROGENEOUS NUCLEATION OF A COMMON ATMOSPHERIC AEROSOL: AMMONIUM SULFATE

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Heterogeneous nucleation of a common atmospheric aerosol: Ammonium sulfate

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Abstract. Natural and anthropogenic aerosols have a direct impact on the earth's radiative balance. Many of the common atmospheric aerosols contain hygroscopic salts and therefore their physical state and composition are sensitive to the relative humidity. The phase of the aerosol particle will dramatically affect the relative rates of atmospheric reactions, and radiative properties such as scattering and optical activity. In order to understand these atmospheric processes and provide accurate input for global modeling, it is imperative that these phase transitions be well defined. It is thought that the degree of metastability is influenced by the presence of foreign particulate matter. These solid impurities are predicted to reduce the barrier of nucleation by providing a surface upon which heterogeneous nucleation can be catalyzed. We report the results of $CaCO_3$ and $BaSO_4$ solid impurities on the efflorescence of $(NH_4)_2SO_4$-H_2O micro-droplets. The results show that both solid impurities act as catalysts for heterogeneous nucleation by causing a decrease in the degree of metastability at the efflorescence point. $BaSO_4$ does not prove to be significantly more efficient than $CaCO_3$ in spite of having the same crystalline structure and similar lattice parameters as in $(NH_4)_2SO_4$.

I. Introduction

A large fraction of atmospheric aerosols contain hygroscopic components; their optical properties tend to be a strong function of the water content. A dry hygroscopic aerosol transforms into a solution droplet when the relative humidity (RH) is increased to the deliquescence point. When the RH is decreased such a droplet becomes metastable (supersaturated) and eventually transforms back to the solid phase at the efflorescence RH, which is much lower than the deliquescence RH. It is estimated that atmospheric aerosols are found in this metastable state close to 50% of the time [*Rood et al.*, 1989]. Optical properties of aerosols at the same RH can be vastly different depending on whether they are solids or liquid droplets. The scattering cross-section of an ammonium sulfate solution droplet at 50% RH is twice the value than when the same aerosol is dry [*Boucher and Anderson*, 1996; *Tang*, 1981]. Therefore, it is imperative to be able to predict the atmospheric conditions under which liquid-solid transitions occur for the estimation of aerosol optical properties.

Deliquescence is an equilibrium phase transition and can be studied in bulk. In contrast, efflorescence transitions occur far from equilibrium, are kinetically controlled, and will therefore depend on sample size. Consequently, efflorescence can only be studied in aerosol form. For the most part, these experiments have concentrated on pure substances. However, studies of ambient aerosol compositions using single particle mass spectroscopy have shown that atmospheric aerosols are typically internally mixed [*Murphy and Thomson* , 1997] and, in the lower troposphere, have been found to contain mixtures of inorganic and organic components. Another common class of internally mixed aerosols was found to be composed of particles from the earth's mantle and hygroscopic inorganic salts [*Wolff et al.*, 1991; *Sloane et al.*, 1991; *Chow et al*., 1994; *Lewis et al*., 1986; *Lewis and Dzumbay*, 1986]. The presence of such solid particles within deliquesced hygroscopic droplets may have a profound effect on the efflorescence behavior. The purpose of the present study was to investigate the effect of solid inclusions on the efflorescence behavior of a common hygroscopic salt found in atmospheric aerosols. In this letter we report on our studies of single suspended $(NH_4)_2SO_4$-H_2O solution droplets containing small (<250nm) $CaCO_3$ or $BaSO_4$ solid inclusions. The results herein describe the effect of these solids on the nucleation behavior of this system. The data show that both solid impurities increase the probability for nucleation and, hence, efflorescence occurs at a higher RH than pure $(NH_4)_2SO_4$. It is important to recognize however, that despite the impurities' presence supersaturation is still observed. In heterogeneous nucleation, the degree of supersaturation is expected to be a strong function of the surface area and its compatibility with the nucleating species. The difference in the degree of supersaturation seen between the two solid catalysts in the present study can, for the most part, be attributed to the differences in relative surface area available for heterogeneous nucleation. No significant enhancement in the nucleation rate is observed with $BaSO_4$ over $CaCO_3$ even though the former possesses a common anion, and belongs to the same crystalline symmetry group as $(NH_4)_2SO_4$.

II. Previous Heterogeneous Nucleation Studies

Early studies on heterogeneous nucleation were predominately based on bulk measurements of various alkali halides crystallizing onto mica substrates [*Upreti and Walton*, 1966; *Newkirk and Turnbull*, 1955]. Most pertinent to the work presented here are the studies of heterogeneous nucleation in suspended ternary solution droplets containing two soluble salts by *Snyder and Richardson* [1993], *Richardson and Snyder* [1994], and *Tang* [1997]. For NaCl-KCl, CsCl-KCl and $NaNO_3$-Na_2SO_4 solutions, a decrease in the maximum supersaturations were seen in the presence of a solid surface whereas with KF-KCl no effect was seen [*Richardson and Snyder*, 1994]. Most recently, *Dougle et al.* [1998] reported the effect of soot on the crystallization of NH_4NO_3 and NH_4NO_3-$(NH_4)_2SO_4$ internally mixed aerosols. In their work, they found that soot impurities did not induce heterogeneous nucleation in either pure NH_4NO_3 or internal mixtures of NH_4NO_3-$(NH_4)_2SO_4$.

III. Experiment

A brief description of the single-particle levitation technique is given here; full details are given elsewhere [*Tang and*

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Munkelwitz, 1994]. Solutions were prepared and filtered three times before introducing them into a particle gun. For the homogeneous case, a 4% (by weight) $(NH_4)_2SO_4$ solution was used to generate a 5-10 µm particle For the heterogeneous case, a saturated homogeneous solution of $CaCO_3$ or $BaSO_4$ containing 4% $(NH_4)_2SO_4$ was prepared. No solid particulate matter was present in the solution when the liquid particle is injected into the chamber. After the particle was centered within the cell, the chamber was evacuated to 10^{-6} torr, at which point the solvent had completely evaporated, and an anhydrous crystalline particle remained. The vapor pressure, temperature within the chamber and the particle's mass were continuously monitored. At the $(NH_4)_2SO_4$ deliquescence point, the particle absorb water, and the $(NH_4)_2SO_4$ fraction will completely dissolve, while only a small fraction of the $BaSO_4$, or $CaCO_3$ does. Therefore, as long as the RH is kept sufficiently low, a solid $BaSO_4$, or $CaCO_3$ particle will be present. The cycle can be completed and the particle returned to a crystalline state, at the efflorescence point, by evacuating the system or decreasing the relative humidity. In contrast to bulk samples, the suspended particle does not effloresce at the same RH as the deliquescence point, but remains in a supersaturated metastable state until the energy barrier for nucleation is surmounted. Both $CaCO_3$ and $BaSO_4$ were chosen for their limited solubility in water ($1.53x10^{-3}$g/ 100cm^3, $2.46x10^{-4}$g/ 100cm^3 [CRC Handbook]), and the high relative humidity both require to deliquesce. In the case of $CaCO_3$, in principle, through a reaction with $(NH_4)_2SO_4$ there is the possibility of $CaSO_4$(s) formation. However, it can be shown on the basis of known solubility constants that the solubility product for the formation of $CaSO_4$(s) is not exceeded and therefore $CaSO_4$ will not be present to act as a heterogeneous catalyst for nucleation.

A seeded ammonium sulfate particle was formed from the supernatant of a dilute $(NH_4)_2SO_4$ solution but saturated with the seed compound. For the two ternary solutions prepared: 4% $(NH_4)_2SO_4$-saturated $CaCO_3$, and 4% $(NH_4)_2SO_4$-saturated $BaSO_4$, the estimated diameters of the insoluble impurities are approximately 225 nm and 100 nm, respectively. It is assumed in this calculation that the seed particle contains no co-precipitated $(NH_4)_2SO_4$. While co-precipitation will effect the size of the seed particle, the magnitude of this effect is negligible in comparison to the relative uncertainty found in the aerosol droplet diameter which spans from 5-10µm. The size of the impurity particle is estimated from the volume of a 5 µm particle ($6.54x10^{-11}$ cm^3), the relative concentrations of the stock solutions of $(NH_4)_2SO_4$ and $CaCO_3$ or $BaSO_4$, the mass of $(NH_4)_2SO_4$ present in the particle, and the mole ratio of $(NH_4)_2SO_4$:H_2O present at the deliquescence point. If the estimated concentrations of $CaCO_3$ or $BaSO_4$ obtained from these values at the deliquescence point exceed their respective solubilities, the excess insoluble salt will be present as a solid. These solid impurities can act as sites for heterogeneous nucleation. The volume of the $CaCO_3$ or $BaSO_4$ seed particle is calculated from the derived excess mass and known densities to yield an impurity diameter. Note this difference in size implies that the surface area of the $BaSO_4$ particle is 5 times smaller than $CaCO_3$.

IV. Results

Figure 1a shows deliquescence-efflorescence cycles for a pure $(NH_4)_2SO_4$-H_2O particle representing the homogeneous nucleation case. The corresponding cycles for the seeded experiments are displayed in Figure 1b and 1c for $BaSO_4$ and $CaCO_3$ respectively. All cycles were performed at 298±1K. The pure $(NH_4)_2SO_4$ trace exhibits sharp, well defined transitions occurring at the deliquescence and efflorescence points at RHs of 80% and 37% respectively, in agreement with previous measurements [*Tang*, 1984; *Xu et al.*, 1998]. Data corresponding to the 225 nm $CaCO_3$ seed shows the typical mixed salt deliquescence behavior: a gradual onset of deliquescence at a lower RH than either pure salt component followed by a sharp dissolution to form a homogeneous solution [*Tang*, 1976; *Tang, Munkelwitz and Davis*, 1978]. In Figure 1b and c, the gradual increase in mass seen before the deliquescence point of pure $(NH_4)_2SO_4$ is due to the increased solubility of $(NH_4)_2SO_4$ in the mixed salt solution. The presence of an insoluble $CaCO_3$ particle is apparent at the efflorescence point, for this case, it is at 48.5%. The 100nm $BaSO_4$ impurity shows the same mixed salt deliquescence behavior as $CaCO_3$ and an efflorescence transition at 45.8% RH. These experiments have been reproduced numerous times with very similar results indicating a spread of ±1.5% in the efflorescence RH. The results indicate:

1. Qualitatively, both insoluble impurities exhibit the same deliquescence behavior seen with soluble mixed salt mixtures;
2. Despite the presence of heterogeneous nucleation sites in these experiments, supersaturation was still required for nucleation;
3. The presence of an impurity decreases the supersaturation needed for nucleation relative to the homogeneous nucleation of pure $(NH_4)_2SO_4$;
4. Nucleation on the smaller (a factor of five in surface area) $BaSO_4$ impurity required higher supersaturation than for the $CaCO_3$.

V. Discussion

The pure $(NH_4)_2SO_4$-H_2O system shows a sharp transition at the deliquescence point whereas, in the heterogeneous case, mixed salts, even if only slightly soluble go through partial dissolution before becoming a homogeneous solution droplet. This is observed as a gradual increase in relative mass as the eutonic mixture dissolves first when the relative humidity is increased. Both soluble and insoluble salt mixtures such as $CaCO_3$ show this behavior, indicating that both have partially dissolved components at the deliquescence point. At the efflorescence point, ternary soluble salt mixtures may exhibit a stepwise crystallization, as in the case of the KCl-NaCl system. Others such as the ternary Na_2SO_4-NaCl-water system exhibit a single nucleation event that occurs at a RH in-between the two pure substance's efflorescence points.

In the insoluble salt case, a solid impurity is present at all times since the relative humidity for the deliquescence of the insoluble salt is never reached. $CaCO_3$, the more soluble of the two insoluble salts, would require a mole $H_2O/(NH_4)_2SO_4$ of ~180. From the deliquescence-efflorescence cycles, it can be estimated that the seed particle will remain until the RH exceeds

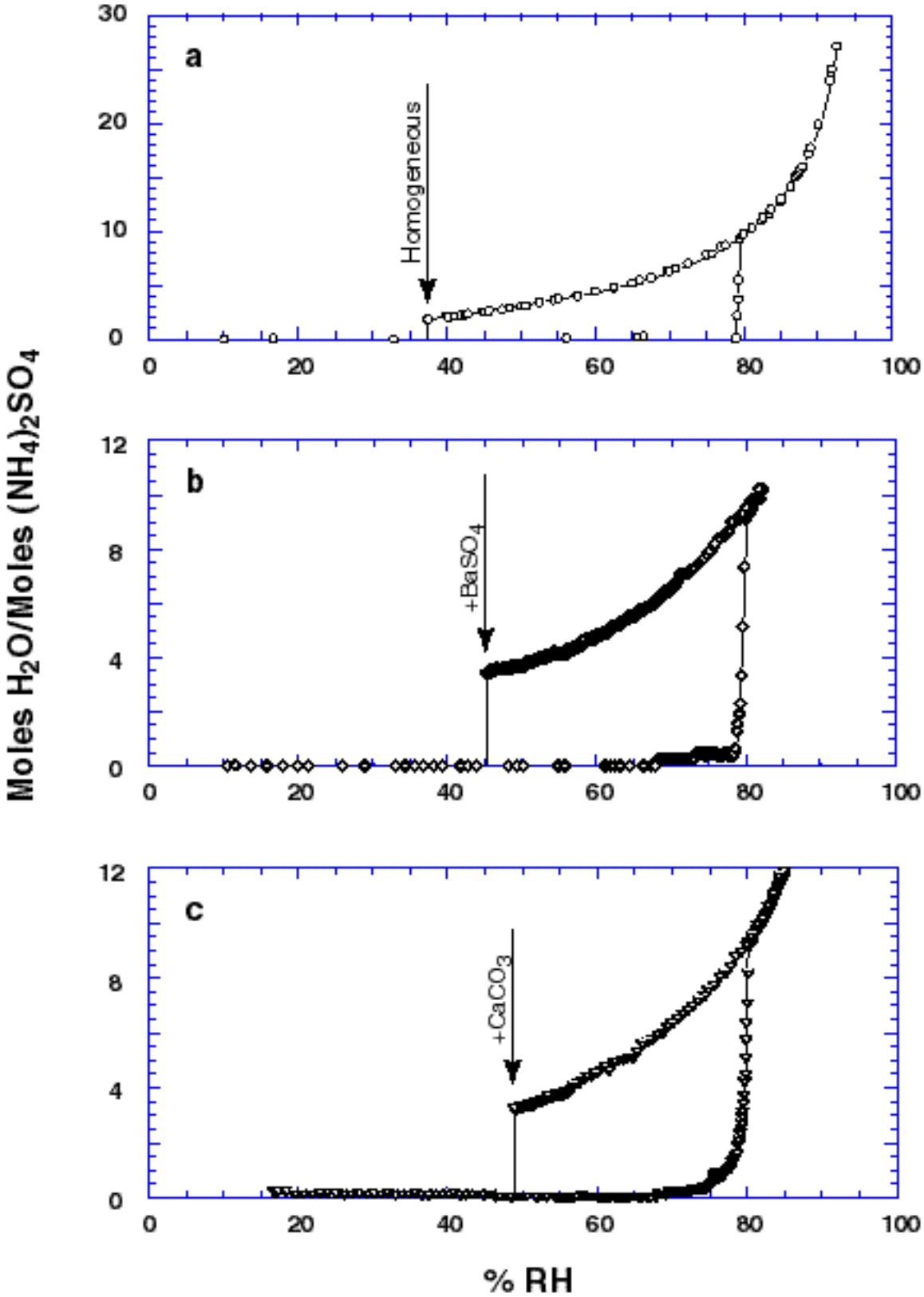

Figure 1. Deliquescence and efflorescence cycles for: a. $(NH_4)_2SO_4/H_2O$; b. $(NH_4)_2SO_4/H_2O$ with a ~100nm $BaSO_4$ particle; c. $(NH_4)_2SO_4$ with a ~225nm $CaCO_3$ particle. Arrows mark the efflorescence points.

95%. A single nucleation event is observed at the heterogeneous nucleation point. In addition to providing a good analogy for realistic atmospheric cases, these systems represent a simple model for studying the phenomenon of heterogeneous nucleation.

The following quantitative treatment is adopted from the work of *Richardson and Snyder* [1994] which examines the heterogeneous nucleation behavior of soluble mixed salts. Within this treatment, the following assumptions have been made: (1) a single nucleation event is observed and initiated from a single critical nucleus; (2) the seed particle is pure $CaCO_3$ or $BaSO_4$. The heterogeneous nucleation rate is proportional to the surface area A of the seed nucleus present in the levitated drop and can be expressed as:

$$J = AJ_o e^{-W^*/kT} \quad (1)$$

[*Richardson and Snyder*, 1994], where W^* is the nucleation barrier height equal to the reversible work required to form the critical nucleus, and the kinetic pre-factor is the product of an intensive factor J_o ($cm^{-2}s^{-1}$) and A . In the present experiments, at the RH of the reported efflorescence points, the nucleation rate is approximately one event per 5 micron particle, per minute. Since A is fixed for each impurity and J_o ($cm^{-2}s^{-1}$) is substrate independent [*Newkirk and Turnbull*, 1955] the nucleation rate can be changed only through W^*, the barrier height. Under the assumptions of classical nucleation theory the barrier height, W^*, and the number of molecules in the critical nucleus, g^*, are homogeneous functions of the excess free energy per molecule of solute, $\Delta\mu_2$ [*McGraw and Laaksonen*, 1996] and can be expressed as follows:

$$W^*_{CNT} / kT = \frac{1}{2} g^* \ln S^* \quad (2)$$

As shown by *Richardson et al*. [1994] S^* the critical supersaturation, can directly be obtained from the data through Gibbs-Duhem integration

$$\ln S^* = -\int_d^e X_2 / X_1 d \ln RH = \frac{\Delta\mu_2}{kT} \quad (3)$$

where X_2/X_1 is the molar ratio of water to $(NH_4)_2SO_4$, and d and e are the RH at the deliquescence and efflorescence points.

The kinetic pre-factors in Equation 1 were estimated to be J_o ($cm^{-2}s^{-1}$) = 1 x 10^{22} and J_o ($cm^{-3}s^{-1}$) = 7 x 10^{31} for the homogeneous and heterogeneous cases respectively [*Newkirk and Turnbull*, 1955]. On the basis of these equations and the observed critical supersaturations we can derive the barrier height, and the number of molecules in the critical nucleus for the nucleation events in the present study. These results are given in Table 1.

Table 1

Case	Impurity Diameter	Nucleation %RH	S^*	W^*_{CNT}/kT	g^*
$(NH_4)_2S0_4$	—	37	25	54	33
$CaCO_3$	225nm	48.5	14	35	27
$BaSO_4$	100nm	45.8	16	33.5	24

The data show that the presence of a solid impurity significantly decreases the critical supersaturation required for crystallization to occur. It also shows a very small difference between the two seeded experiments, in which the smaller seed required slightly higher supersaturation as one would expect on the basis of surface area alone. When comparing the two heterogeneous nucleation cases it would be reasonable to expect that the differences might be dominated by the mismatch between the $(NH_4)_2SO_4$ and seed crystal structures.

Although the preceding analysis does not require a specific model for the heterogeneous nucleus, an analysis can be carried out using the well-known spherical cap model (e.g., *Richardson and Snyder*, 1994). We find that the three sets of measurements in Table 1 are consistent with embryo/substrate contact angles of 86 degrees and 87 degrees for $CaCO_3$ and $BaSO_4$, respectively. While the spherical cap model may not be reliable for formation of a crystalline nucleus consisting of only a few unit cells (Table 2), the closeness of these angles suggests that the two different substrates have similar affinity for inducing crystallization under the conditions of the measurements.

Table 2

Case	Z^1	a_o^2	b_o^2	C_o^2	Space group
$(NH_4)_2SO_4$	4	7.78	5.99	10.64	D^{16}_{2h}
$CaCO_3$	6	4.99	—	17.06	D^{6}_{3d}
$BaSO_4$	4	8.87	5.45	7.15	D^{16}_{2h}

[1] number of molecules in a unit cell; [2] size of unit cell in Angstrom.

Table 2 provides a comparison between the crystal parameters for the impurities and $(NH_4)_2SO_4$. $(NH_4)_2SO_4$ and $BaSO_4$ have an orthorhombic crystalline structure with 4 molecules to a unit cell lattice, mismatches of about 0.5 and 1 angstrom. $CaCO_3$, on the other hand, belongs to a different symmetry group and has a very different crystalline structure. Despite this, the data suggest that $BaSO_4$ is not that much more efficient at nucleating $(NH_4)_2SO_4$ than $CaCO_3$.

VI. Conclusion

We presented a study of the effect of solid inclusions, of representative character and size of mineral dust and other crustal material, on the efflorescence behavior of $(NH_4)_2SO_4$ aerosols. The supersaturation of $(NH_4)_2SO_4$ is obtained experimentally from the measured RH and levitated droplet mass using Gibbs-Duhem integration. It was found that the inclusions serve to significantly lower the critical supersaturation of $(NH_4)_2SO_4$ relative to that required for homogeneous nucleation to take place. In our study, the fact that no significant difference in the efficiency of nucleation between the $CaCO_3$ and $BaSO_4$ substrates was observed does not preclude such an effect from occurring in other cases. These preliminary results highlight the need for a comprehensive study to include systematic variation of seed areas and supersaturation for a variety of hydroscopic salts and inclusions.

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