
CRYSTALLIZATION OF $(\text{NH}_4)_2\text{SO}_4$ DROPLETS AT LOW SUPERSATURATIONS IN THE ATMOSPHERE

Ravi Kumar

Department of Chemistry
Multanmodal Modi College, Modinagar

ABSTRACT:

The crystallisation of ammonium sulphate was investigated over a range of humidities using microscope system. From the experiments nucleation rates were determined which are consistent with the literature report for a weaker rate dependence on relative humidity (RH) at high RH corresponding to low super saturations for ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$). Isohumid experiments carried out above the efflorescence RH (ERH) of ammonium sulphate (~37%) were used to investigate the low super saturation region. The results were consistent with reports from the literature and may be due to formation of a different crystalline phase at high RH.

KEYWORDS: Nucleation-----Saturations--- $(\text{NH}_4)_2\text{SO}_4$ ----DRH---ERH---crystallization

INTRODUCTION

Atmospheric aerosols provide solid nuclei for cloud formation. The presence of hygroscopic salts such as ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$) in aerosols allow them to exist as aqueous droplets and hence affect their nucleation properties. The concentration and phase of aqueous $(\text{NH}_4)_2\text{SO}_4$ aerosols is governed in part by relative humidity (RH). At RH below the deliquescence point $(\text{NH}_4)_2\text{SO}_4$ droplets become supersaturated. Further lowering of RH causes $(\text{NH}_4)_2\text{SO}_4$ to effloresce out of solution at a rate proportional to the RH. Several studies (Mullin and Ang, 1976; Sohnle and Mullin, 1978; Hendriksen and Grant, 1995; Pant et al., 2006; Parsons et al., 2006) show that this dependence is weaker at low super saturations. In the most recent studies this has been attributed to impurities heterogeneously nucleating efflorescence (Pant et al., 2006; Parsons et al., 2006). By using ultra pure $(\text{NH}_4)_2\text{SO}_4$ solutions and slides coated with dichlorodimethylsilane (DMS) it was intend to rule out heterogeneous nucleation. If weaker dependency at low super saturations persists, $(\text{NH}_4)_2\text{SO}_4$ may be efflorescing homogeneously into a different phase at higher RH. Consequently pure $(\text{NH}_4)_2\text{SO}_4$ droplets may provide solid nuclei for cloud formation on timescales relevant to the atmosphere over a larger RH range than previously thought.

A hygroscopic solid crystal will take up water at its deliquescence humidity (DRH). This is defined by equation (1) when the saturation ratio of the solute (S_{solute}) is equal to 1:

$$S_{\text{solute}} = \frac{C_{\text{solute}}}{C_{\text{solute}}^*} \quad (1)$$

where C_{solute} is the concentration of solute in the solution, and C_{solute}^* is the concentration of solute in a saturated solution in equilibrium with a solid crystal of that solute. Since C_{solute} is inversely proportional to water activity, a_w , and hence RH ($100 \times a_w$), the deliquescence point can be defined in terms of RH. It should be noted that the DRH is also temperature dependent and so should be defined for a particular temperature. The temperature dependence of the DRH for $(\text{NH}_4)_2\text{SO}_4$ particles is described by Tang *et al.* who quote a DRH of 79.9% at 298K (Tang and Munkelwitz, 1993). a_w is defined as:

$$a_w = \frac{p_{H_2O}}{p_{liq}^*} \quad (2)$$

Where p_{H_2O} is the partial pressure of water vapour outside the droplet, and p_{liq}^* is the vapour pressure of liquid water. The coefficient of proportionality between a_w and C_w (the concentration of water in the solution) at a given a_w , is the activity coefficient γ of the solution:

$$a_w = \gamma \cdot C_w \quad (3)$$

and as the concentration of water in the solution increases, that of the solute decreases (i.e. the solution becomes more dilute) it can be said that:

$$a_w = \frac{\gamma}{C_{\text{solute}}} = \frac{RH}{100} \quad (4)$$

And hence that

$$S_{\text{solute}} = \frac{\gamma}{a_w \cdot C_{\text{solute}}^*} = \frac{\gamma}{RH \cdot C_{\text{solute}}^*} \times 100 \quad (5)$$

Therefore by varying RH, the saturation ratio of the solute can be varied, and thus the concentration and phase of the aqueous solution. To work out S from the RH, γ and C_{solute}^* must be known. γ can be complex to calculate as it depends on other factors such as the solubility and chemical potential of the ions involved. Here the Clegg model (Clegg et al., 1998; Clegg, 2002) will be used to calculate γ , thus allowing us to calculate C_{solute}^* , which is C_{solute} when $S_{\text{solute}}=1$, and hence S_{solute} .

As the RH is lowered passed the DRH, C_{solute} becomes greater than C_{solute}^* , i.e. $S>1$, but the solute does not immediately effloresce back out of solution. Instead the solution forms a metastable supersaturated solution, and will only effloresce at a much lower humidity. The efflorescence humidity (ERH) of $(\text{NH}_4)_2\text{SO}_4$ is around 37% RH as opposed to the DRH of 79.9% as shown in figure 1.

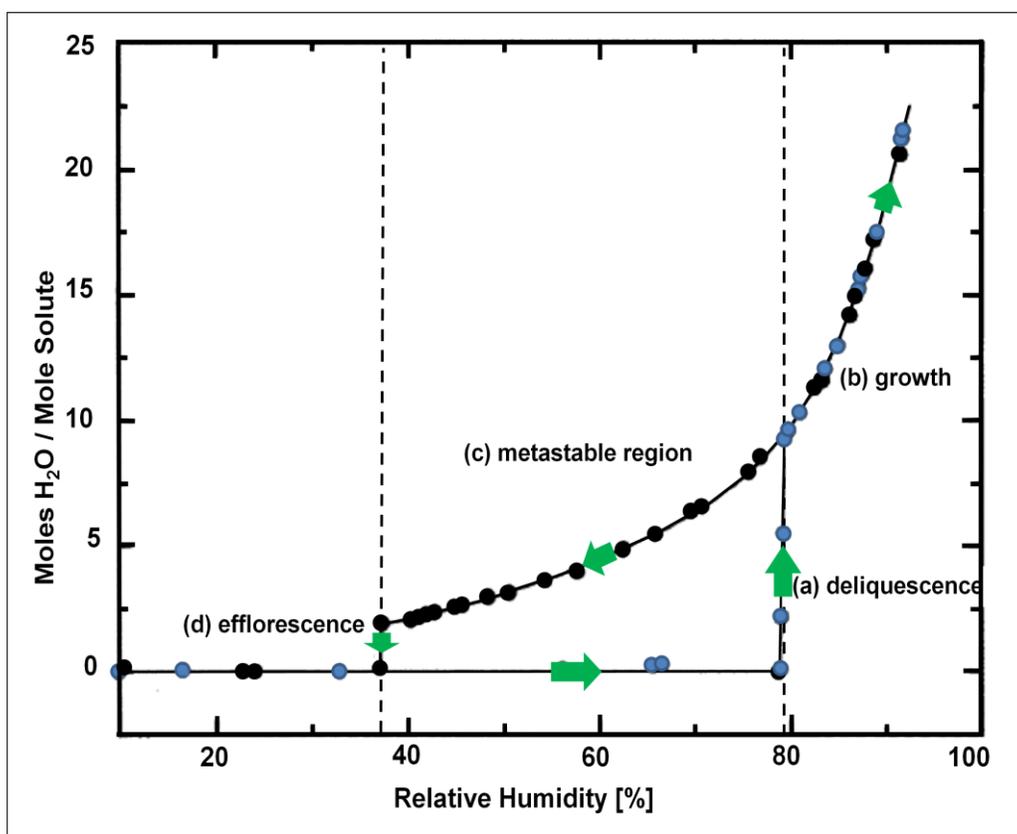


Figure 1 Deliquescence and Efflorescence of $(\text{NH}_4)_2\text{SO}_4$ (Tang et al., 1995).

EXPERIMENTAL:

Slide preparation

Glass slides (0.3 mm thick, 13 mm diameter) were first soaked in piranha solution (40 ml, $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ 3:1) for at least 40 minutes to remove organic residues that may be present on the slide surface. They were then washed with water (18.2 M Ω), methanol (analytical grade), and chloroform (analytical grade) and dried using dry N_2 gas. The washed slides were placed in clean jars in batches of five. To prevent the surface of the

slides from causing heterogeneous nucleation, a drop of silanising solution (6% dichloromethylsilane in hexane) was added to each jar and the jars were left overnight. The volatile dichloromethylsilane transfers to the glass slide *via* the vapour phase. The silane group reacts with an OH group on the surface of the glass which forms a covalent bond. These results in the glass being directly bound to hydrophobic silane groups and as such, it is very robust way of making the slide surface hydrophobic. The hydrophobicity of the surface ensures minimum contact between the slide and the droplets. The resulting contact angle between the slide and the droplets was estimated at 10° based on past measurements (Koop et al., 1998; Dymarska et al., 2006; Knopf and Koop, 2006; Eastwood et al., 2009; Knopf and Lopez, 2009). In order to obtain droplets of an atmospherically relevant size a homemade nebuliser was used to administer solution droplets to the slide surface.

Prior to use one vial worth of water (~15 ml) was run through the nebuliser to get rid of any particulates that may have built up in the tubing. The needle from the nebuliser was placed through the septum of the vial containing the sample solution. The slide to be nebulised was placed in the neck of the chamber and a plastic bag surrounding the neck was loosely sealed. Dry N_2 gas was fed into the nebuliser at a pressure of ~1.6 bar. This siphoned the solution rapidly through the end of the thin pipette and into the chamber resulting in a fine mist. Each slide was exposed to the nebulised solution in this manner for ~45 s, resulting in a distribution of droplets 2-40 μ m in size on the slide surface.

After nebulisation of the slide with the sample solution, the slide was quickly transferred to the stage shown in figure 2 and sealed inside the Perspex chamber. The temperature of the stage is controlled by heaters embedded within it which heat against constant cooling supplied by liquid nitrogen circulating around the stage. The temperature of the stage is measured by thermocouples which are positioned directly under the droplets. To ensure that the reading given by the thermocouples was representative of the temperature within the droplets the sample slide was placed directly on top of a highly thermally conducting sapphire disc which was stuck to the stage with thermal grease, thus minimising any temperature gradient between the thermocouples and the droplets. Before each experiment all thermocouples were calibrated in an ice-water bath. Nucleation events were observed *via* the optical microscope and the footage was recorded to DVD for analysis.

A 20 wt% $(NH_4)_2SO_4$ solution will be made up using highly pure 18.2 M Ω water. To get droplets of a size comparable to that found in the atmosphere the solution will be nebulised onto thin glass slides. Prior to nebulisation the glass slides must be cleaned thoroughly to remove any foreign particles. This is done by soaking them in Piranha solution (H_2O_2 and H_2SO_4 in a 1:3 ratio) for at least 40 minutes). They are then washed in 18.2 M Ω water, methanol, and chloroform and dried with dry N_2 gas. Finally they are placed in clean jars. To prevent the surface of the slides from heterogeneously nucleating efflorescence, a drop of dichlorodimethylsilane is placed in each jar, and overnight vaporises and condenses onto the surface of each slide creating a monolayer of non-polar hydrophobic silane groups on each slide which ensures minimum contact between the slides and the droplets.

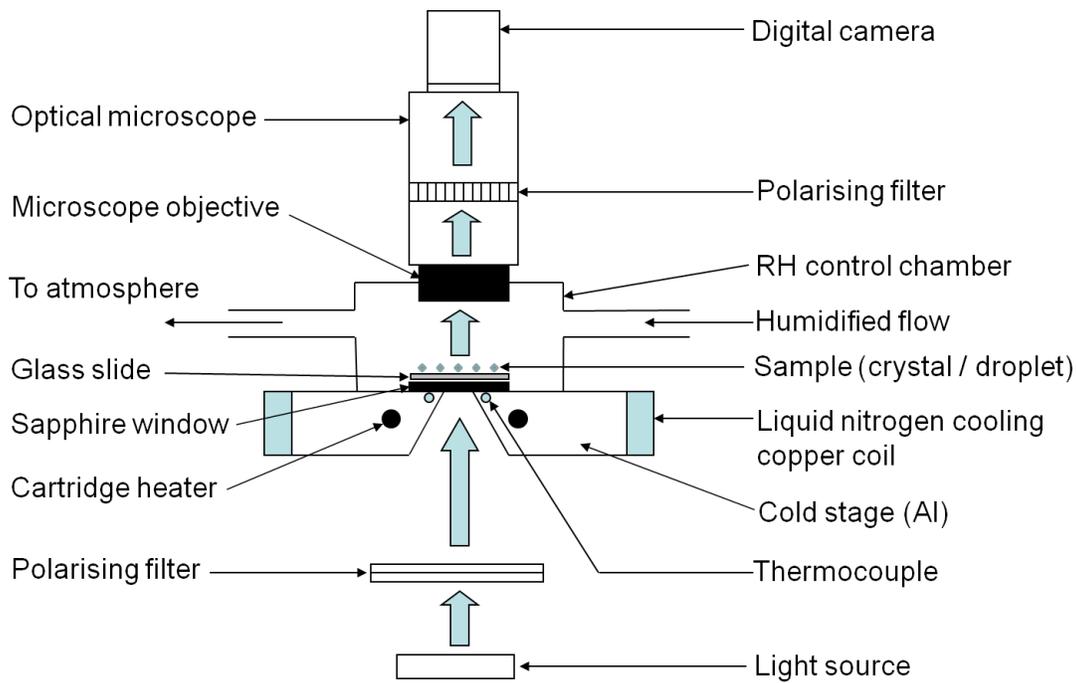


Figure 2 Experimental setup for crystallisation experiments based on an original design by Koop *et al.* (Koop *et al.*, 1998) and adapted for these experiments

RESULTS AND DISCUSSIONS

Footage of each run was recorded to DVD. From the footage the time that each droplet crystallised and the size of each droplet upon crystallization were recorded. This information was later used to calculate the nucleation rates. Figure 3 shows a typical run for ammonium sulphate at different stages. Crystallisation events can clearly be observed as the centre of a droplet changes from translucent to black.

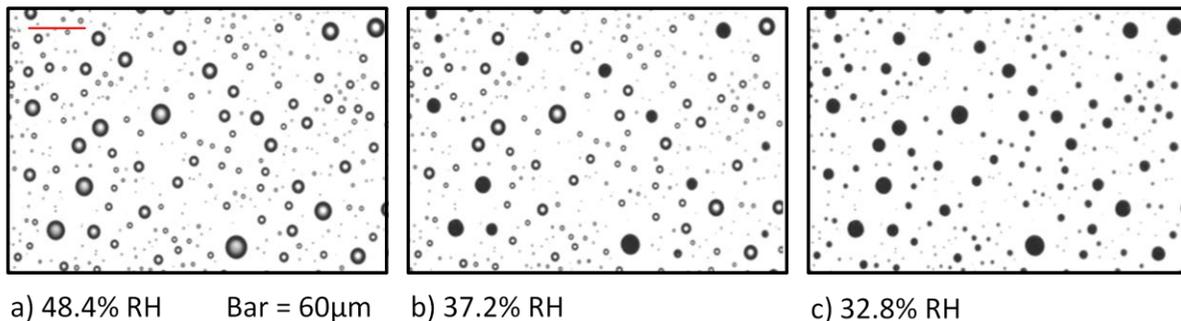


Figure 3. Images a typical run for ammonium sulphate droplets (ASR=2). (a) all droplets are liquid, (b) some of the droplets have crystallised, (c) all the droplets have crystallised.

In ammonium sulphate droplets crystallisation is a rapid procedure, an entire droplet crystallising in a fraction of a second. However, as the ASR was decreased, the droplets became more viscous and consequently crystallisation of the entire droplet became slower. For this reason it became increasingly difficult to determine the exact point of nucleation especially in the smaller droplets. This can be seen from stills of the video footage for the ASR=1.3 run shown in figure 4:

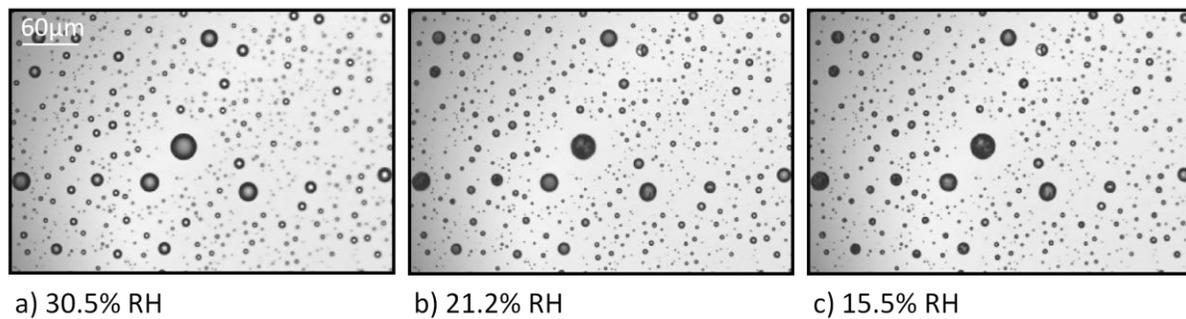


Figure 4. Images the run conducted at ASR=1.3. (a) all liquid, (b) some liquid, some solid and (c) all solid. To prevent any error in the nucleation times recorded, for the ASR=1.4 run all droplets smaller than 7 μm in size were ignored, and for the ASR=1.3 run, all droplets smaller than 8 μm were ignored. The actual size of the droplets was determined by using a stage micrometer. This was put under the microscope and filmed at the same magnification as the droplets. The footage was recorded to DVD and played on the computer screen on which the analysis was being conducted, thus allowing a scaling factor to be determined.

EFFLORESCENCE RELATIVE HUMIDITY (ERH)

From each run the ERH could be determined by plotting the fraction of droplets crystallized against the RH of crystallization (figure 5). The resulting trend was an S-curve as at high RH the nucleation rate was slow and so only a few droplets crystallized. As the RH was lowered, the rate of nucleation increased slowly at first and then dramatically, the majority of droplets crystallizing over a small RH range. Once most of the droplets had crystallized a slight tail is seen as crystallization becomes statistically less likely because the number of droplets left uncrystallized is so small.

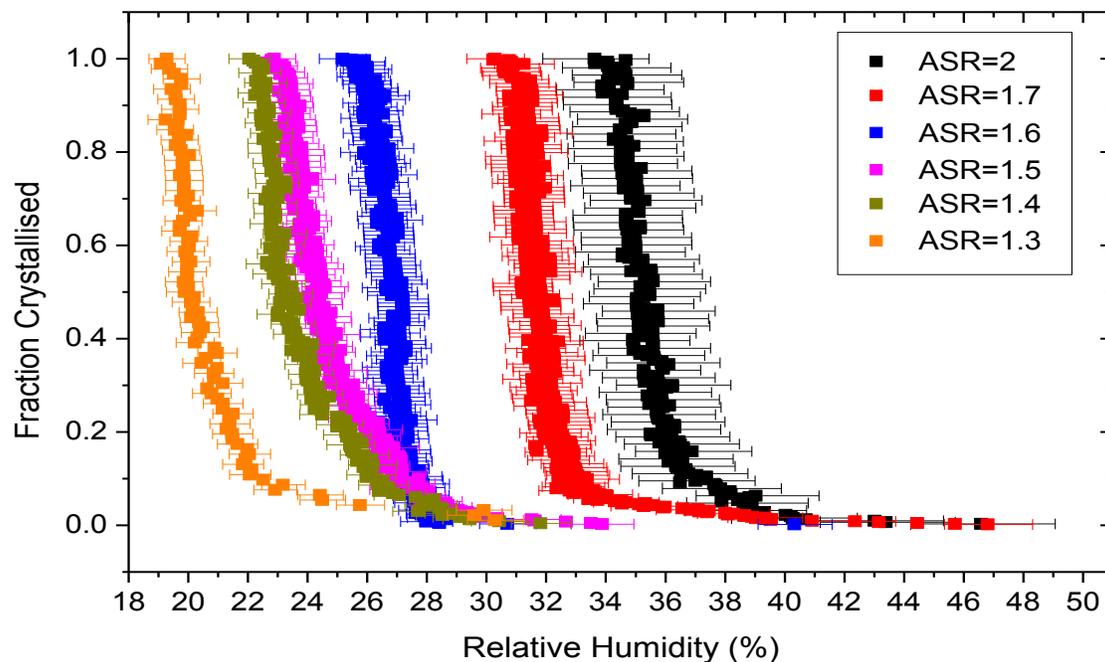


Figure 5. S-curves for a series of different ASR runs. The characteristic S-shape is due to low nucleation rate at high humidity, high nucleation rate at low humidity and statistically low chance of crystallisation when most droplets have crystallised. Note that some error bars have been removed for clarity.

Figure5 shows that as the ASR in the $(\text{NH}_4)_2\text{SO}_4$ droplets decreases, the ERH also decreases as expected. Table-1 shows the ERH for each run with literature values for comparison. In these experiments the ERH was define as the RH at which 50% of the droplets have crystallized:

ASR	ERH (%)	Temperature (K)	Reference
2	35.2	293.2	Current data
	37	298	(Tang et al., 1995)
	32	294.8	(Onasch et al., 1999)
	35	298	(Han and Martin, 1999)
	33	298	(Cziczo et al., 1997)
	36	298	(Tang, 1980)
1.7	31.4	293.2	Current data
1.6	26.8	293.2	Current data
1.5	24.2	293.2	Current data
	27.5	263.5	(Colberg et al., 2004)
1.4	23.1	293.2	Current data
1.3	19.9	293.2	Current data

Table 1 Comparison of ERH for a range of ASRs measured here and in the literature.

CONCLUSIONS:

The ERH of ammonium sulphate determined here (35.2%) falls within the range of ERHs determined for ammonium sulphate in the literature. There is some scatter in these results which is unsurprising as the ERH depends upon the temperature at which the experiment was carried out, the size of the droplets, the presence of any impurities which may cause heterogeneous nucleation, and the time over which the experiment was conducted. For isohumid runs conducted, the crystallization of 50% of the droplets was observed as high as 39% RH when left at this RH for over 10 hours. The discrepancy between the two values is likely due to the large difference in temperature at which the two experiments were conducted. The reason that ERH decreases with ASR is probably due to the fact that the viscosity of the droplets increases with a decrease in ASR making it less favourable for water to evaporate from the droplet.

ACKNOWLEDGEMENTS

Author is grateful to the Government of India for funding and Principal, Multanimal Modi College, Modinagar (U.P.) for support and providing infrastructure and facility to carry out the work.

REFERENCES

1. Clegg, S.L., Brimblecombe, P., Wexler, A.S., 1998. Thermodynamic model of the system $\text{H}^+-\text{NH}_4^+-\text{SO}_4^{2-}-\text{NO}_3^--\text{H}_2\text{O}$ at tropospheric temperatures. *J. Phys. Chem. A* 102, 2137-2154.
2. Clegg, S.L.B., P.; Wexler, A. S., 2002. Extended AIM Aerosol Thermodynamics Model.
3. Colberg, C.A., Krieger, U.K., Peter, T., 2004. Morphological investigations of single levitated $\text{H}_2\text{SO}_4/\text{NH}_3/\text{H}_2\text{O}$ aerosol particles during deliquescence/efflorescence experiments. *Journal of Physical Chemistry A* 108, 2700-2709.
4. Cziczo, D.J., Nowak, J.B., Hu, J.H., Abbatt, J.P.D., 1997. Infrared spectroscopy of model tropospheric aerosols as a function of relative humidity: Observation of deliquescence and crystallization. *Journal of Geophysical Research-Atmospheres* 102, 18843-18850.

5. Dymarska, M., Murray, B.J., Sun, L.M., Eastwood, M.L., Knopf, D.A., Bertram, A.K., 2006. Deposition ice nucleation on soot at temperatures relevant for the lower troposphere. *Journal of Geophysical Research-Atmospheres* 111.
6. Eastwood, M.L., Cremel, S., Wheeler, M., Murray, B.J., Girard, E., Bertram, A.K., 2009. Effects of sulfuric acid and ammonium sulfate coatings on the ice nucleation properties of kaolinite particles. *Geophysical Research Letters* 36.
7. Han, J.H., Martin, S.T., 1999. Heterogeneous nucleation of the efflorescence of $(\text{NH}_4)_2\text{SO}_4$ particles internally mixed with Al_2O_3 , TiO_2 , and ZrO_2 . *Journal of Geophysical Research-Atmospheres* 104, 3543-3553.
8. Hendriksen, B.A., Grant, D.J.W., 1995. The effect of structurally related substances on the nucleation kinetics of paracetamol (acetaminophen). *J. Cryst. Growth* 156, 252-260.
9. Knopf, D.A., Koop, T., 2006. Heterogeneous nucleation of ice on surrogates of mineral dust. *Journal of Geophysical Research-Atmospheres* 111.
10. Knopf, D.A., Lopez, M.D., 2009. Homogeneous ice freezing temperatures and ice nucleation rates of aqueous ammonium sulfate and aqueous levoglucosan particles for relevant atmospheric conditions. *Physical Chemistry Chemical Physics* 11, 8056-8068.
11. Koop, T., Ng, H.P., Molina, L.T., Molina, M.J., 1998. A new optical technique to study aerosol phase transitions: The nucleation of ice from H_2SO_4 aerosols. *Journal of Physical Chemistry A* 102, 8924-8931.
12. Mullin, J.W., Ang, H.M., 1976. Nucleation characteristics of aqueous nickel ammonium-sulfate solutions. *Faraday Discuss.* 61, 141-148.
13. Onasch, T.B., Siefert, R.L., Brooks, S.D., Prenni, A.J., Murray, B., Wilson, M.A., Tolbert, M.A., 1999. Infrared spectroscopic study of the deliquescence and efflorescence of ammonium sulfate aerosol as a function of temperature. *Journal of Geophysical Research-Atmospheres* 104, 21317-21326.
14. Pant, A., Parsons, M.T., Bertram, A.K., 2006. Crystallization of aqueous ammonium sulfate particles internally mixed with soot and kaolinite: Crystallization relative humidities and nucleation rates. *J. Phys. Chem. A* 110, 8701-8709.
15. Parsons, M.T., Riffell, J.L., Bertram, A.K., 2006. Crystallization of aqueous inorganic-malonic acid particles: Nucleation rates, dependence on size, and dependence on the ammonium-to-sulfate. *J. Phys. Chem. A* 110, 8108-8115.
16. Sohnel, O., Mullin, J.W., 1978. Method for determination of precipitation induction periods. *J. Cryst. Growth* 44, 377-382.
17. Tang, I.N., 1980. Generation of aerosols and facilities for exposure experiments. Ann Arbor Science Publishers, MI.
18. Tang, I.N., Fung, K.H., Imre, D.G., Munkelwitz, H.R., 1995. Phase-transformation and metastability of hygroscopic microparticles. *Aerosol Science and Technology* 23, 443-453.
19. Tang, I.N., Munkelwitz, H.R., 1993. Composition and temperature-dependence of the deliquescence properties of hygroscopic aerosols. *Atmospheric Environment Part a-General Topics* 27, 467-473.