Investigating Freezing Point Depression and Cirrus Cloud Nucleation Mechanisms Using a Differential Scanning Calorimeter

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S *Supporting Information*

ABSTRACT: A differential scanning calorimeter was used to study homogeneous nucleation of ice from micron-sized aqueous ammonium sulfate aerosol particles. It is important to understand the conditions at which these particles nucleate ice because of their connection to cirrus cloud formation. Additionally, the concept of freezing point depression, a topic commonly encountered in undergraduate science courses, was experimentally studied using an instrumental technique. As expected, when the concentration of ammonium sulfate in the particles increased, their freezing and melting temperatures decreased. The data was consistent with previous work that showed water activity is the determinant for homogeneous ice nucleation in aerosol particles. This laboratory experiment is appropriate for students enrolled in upper division atmospheric science, chemistry and instrumental analysis courses.

KEYWORDS: *Calorimetry/Thermochemistry, Atmospheric Chemistry, Second-Year Undergraduate, Upper-Division Undergraduate, Analytical Chemistry, Environmental Chemistry, Laboratory Instruction, Physical Chemistry*

INTRODUCTION

Colligative properties of solutions such as freezing point depression are concepts commonly discussed in undergraduate science courses. It is necessary to develop an upper division, undergraduate laboratory experience that demonstrates how various solutes affect colligative properties. A differential scanning calorimeter (DSC) is an instrument used to accurately measure heat flows associated with thermal transitions in materials. Therefore, it is appropriate to use a DSC to study the thermal properties of solutions. For example, undergraduate chemistry students utilized a DSC to determine the molar mass of a substance by measuring its freezing point depression.[1]

In the area of atmospheric sciences, freezing point depression is a concept necessary to understand the formation of ice in the atmosphere. Cirrus clouds, which are composed of ice, are important for climate because they are optically thin in the visible wavelength range. Therefore, they allow most of the incoming solar radiation to reach the Earth's surface. In contrast, they are strong infrared absorbers and contribute to greenhouse warming. It is important to determine temperatures at which cirrus clouds form to understand their effect on the global radiation budget.

Atmospheric aerosol particles are defined as solid or liquid particles suspended in air with diameters between ∼0.002 and 100 μm. Micrometer-sized aqueous atmospheric aerosol particles can serve as ice crystal nuclei which are crucial for cirrus cloud formation. Laboratory experiments have been designed to determine the temperatures at which ice nucleates from aqueous aerosol particles (homogeneous nucleation). For example, Knopf and Rigg[2] studied homogeneous ice nucleation in aqueous droplets (mimicking biomass burning aerosol) with an ice nucleation/optical microscope apparatus. This type of experiment could be carried out by undergraduate students.

Koop et al.[3] utilized a variety of experimental data, including data generated using a DSC, to show water activity is the determinant for homogeneous ice nucleation. Thus, the freezing temperatures of aqueous aerosol particles are affected by the amount of dissolved solute and not its chemical identity. The Koop et al.[3] homogeneous ice nucleation model is important because it simplifies the data necessary to simulate cirrus cloud nucleation in global-scale three-dimensional climate models.

This article describes an experiment designed to demonstrate cirrus cloud nucleation mechanisms through experimental measurements of the freezing point depression and water activity of small aqueous particles. Specifically, this experiment shows the effect water activity (solute concentration) has on the temperature at which aqueous aerosol particles homogeneously nucleate ice. With the use of a DSC, homogeneous ice nucleation from micrometer-sized ammonium sulfate solution particles was performed and the data verified by reference to Koop et al.[3] Ammonium sulfate was chosen as the solute because it is soluble in water, ubiquitous in the atmosphere and economical.

COURSE APPLICABILITY AND LEARNING GOALS

This experiment is appropriate for undergraduate students enrolled in upper division atmospheric science, physical chemistry and instrumental analysis courses. If used in an atmospheric science course, the experiment is appropriate when discussing cloud physics. In a physical chemistry course, the concepts of freezing point depression, boiling point elevation,

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and water activity are important. Therefore, the experiment can be completed after presenting topic of water activity. A DSC is an instrument commonly found in analytical chemistry laboratories. This experiment is suitable when discussing thermal methods of analysis.

The learning goals of the experiment are as follows. Undergraduate science students rarely get the opportunity to read peer-reviewed journal articles in their lecture-based courses. To give students more experience reading journal articles, this experiment is presented in a style mimicking an experimental research paper. The Supporting Information provides several additional references extending the introduction in this manuscript. To more fully understand the topic presented here, the students are expected to read the referenced articles. The experiment combines a modeling and a laboratory component. A learning goal of the experiment is to model the conditions under which micrometer-sized, aqueous particles homogeneously nucleate ice. Therefore, the Koop et al.[3] homogeneous ice nucleation model is constructed prior to laboratory measurements. Finally, the Koop et al.[3] model is used to validate the measured freezing and melting temperatures of micrometer-sized aqueous ammonium sulfate particles.

■ EXPERIMENTAL PROCEDURES

Homogeneous ice nucleation from emulsified, micrometer-sized aqueous ammonium sulfate particles was performed using a Q20 DSC (TA Instruments). The DSC temperature calibration was verified by measuring the melting point of Indium metal (~429.7 K). An additional check of the temperature calibration was carried out at low temperatures by measuring the ferroelectric phase transition of bulk ammonium sulfate (~223.0 K).[4,5]

After the DSC temperature calibration was verified, aqueous ammonium sulfate solutions containing various amounts of solute were emulsified in a mineral oil/lanolin matrix according to a procedure modified from Pinti et al.[6] First, aqueous ammonium sulfate/mineral oil/lanolin samples were created using double distilled water, ammonium sulfate (≥99.0%), mineral oil (100% saturated hydrocarbon) and lanolin (<0.1% water). All compounds were purchased from Sigma-Aldrich. The composition of each sample (by weight) was 76% mineral oil, 4% lanolin and 20% aqueous ammonium sulfate. For each freezing experiment, mixing various amounts of ammonium sulfate in water changed the composition of the aqueous aerosol particles. The water activity of each ammonium sulfate solution was calculated using Model II of the Extended Aerosol Inorganics Model.[7]

Each sample was emulsified using an ultrasonic homogenizer (Omni International Sonic Ruptor 400) for 15 min at 50% power. If the solutions were stored for more than 20 min, they were homogenized again to ensure the micrometer-sized droplets did not coagulate. A volume of 15 μL of an emulsified sample was added to a Tzero pan (using a 5−50 μL adjustable volume pipet) and the pan was sealed with a Tzero hermetic lid using a press (TA Instruments).

The pan was placed in the DSC (maintained at 40 °C) and the sample temperature was reduced (using a RCS90 refrigeration system) at a rate of a 10 K/min until the sample froze. The freezing temperature was defined by the intersection of the tangent line drawn at the inflection of the exothermic signal recorded by the DSC during the phase change with an extrapolated baseline.[6] Once the sample froze, the temperature

was reduced an additional 5 K to recover the baseline signal. Next, the temperature was raised at a rate of 10 K/min until the sample melted. The melting point was defined as the peak in the endothermic signal recorded by the DSC during the phase change.[8] The experiment was completed when the sample returned to room temperature. TA Instruments Universal Analysis 2000 software was utilized to aid in the determination of freezing and melting points.

■ HAZARDS

Ammonium sulfate may cause allergic skin reactions and eye irritation. It is hazardous if ingested or inhaled. Lanolin may cause allergic skin reactions and digestive tract irritation. Mineral oil is slightly hazardous in case of eye contact or it is ingested. Mineral oil is also flammable. Ear protection should be worn while operating the sonicator. The chemicals used in this laboratory are fairly safe; however, it is recommended that protective eyewear and nitrile gloves be worn during sample preparation. Waste should be disposed of according to OSHA safety regulations.

■ RESULTS AND DISCUSSION

Modeling the Homogeneous Melting and Freezing Temperatures of Micrometer-Sized Particles

The melting temperatures (T_m) of aqueous ammonium sulfate particles (represented by the dotted line in Figure 1) are
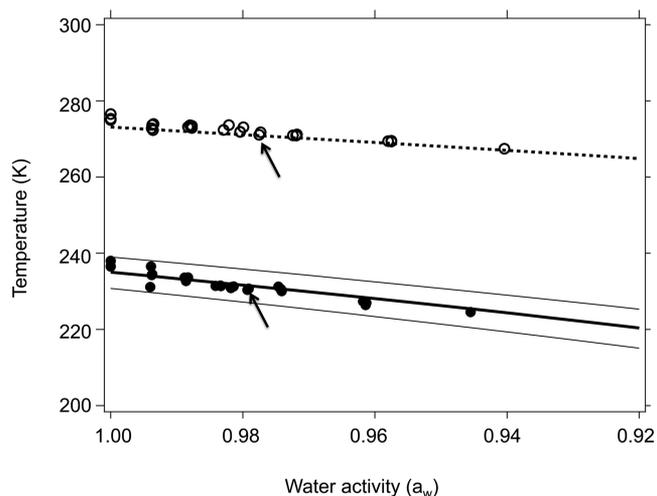
Figure 1. Freezing (filled circles) and melting (open circles) temperatures of aqueous, micrometer-sized ammonium sulfate particles as a function of water activity (a_w). The dotted line represents melting temperatures (T_m) and the thick solid line represents freezing temperatures (T_f) from Koop et al.[3] The thin solid lines denote the error in the Koop et al.[3] freezing temperatures. The arrows pointing to the filled and open circles are the freezing and melting points shown in Figures 2 and 3 respectively.

identical to those in Koop et al.[3] They are calculated assuming the water activity of the ammonium sulfate solution (a_w) is in equilibrium with the activity of ice (a_w^i). Thus, the curves plotted in Figure 1 are ice/water activities at various temperatures. Specifically, a_w^i values in Figure 1 are calculated using the following equations. Equation 1 is used to calculate the vapor pressure of ice (in Pa) between 169 and 273 K.[9]

$$P_{ice} = \exp\left(28.868 - \frac{6132.9}{T}\right) \tag{1}$$

where P_{ice} is the vapor pressure of ice at temperature (T) in Kelvin. Equation 2 is used to calculate the vapor pressure of water (in Pa) between 150 and 273 K.[10]

$$P_{water} \approx P_{ice} \exp\frac{-\left(a + bT - \frac{c}{T} - d\ln(T)\right)}{RT} \tag{2}$$

where P_{water} is the vapor pressure of water, $a = 210368$, $b = 131.438$, $c = 3.32373 \times 10^6$, $d = 41729.1$, and R is the ideal gas law constant (8.314 J/mol K). The water activity of ice is calculated using eq 3.

$$a_w^{\,i} = \frac{P_{ice}}{P_{water}} \tag{3}$$

Homogenous freezing temperatures (T_f, represented by the thick solid line in Figure 1) are calculated assuming T_f is horizontally parallel to T_m and offset by a constant value of 0.305 so T_f intersects the y-axis at 235 K when $a_w^{\,i} = 1$. This is termed the water-activity criterion for homogeneous ice nucleation.[3] The thin solid lines in Figure 1 (water activity offsets of ± 0.025 from T_f) represent uncertainty in the freezing temperatures.[3,11]

Freezing and Melting of Micrometer-Sized Aqueous Ammonium Sulfate Particles

Figure 2 is a thermogram generated using 8.0 wt % ($a_w \sim 0.9793$) aqueous ammonium sulfate particles as temperature

8.0 wt %
a_w = 0.9793
T_f = 230.4 K
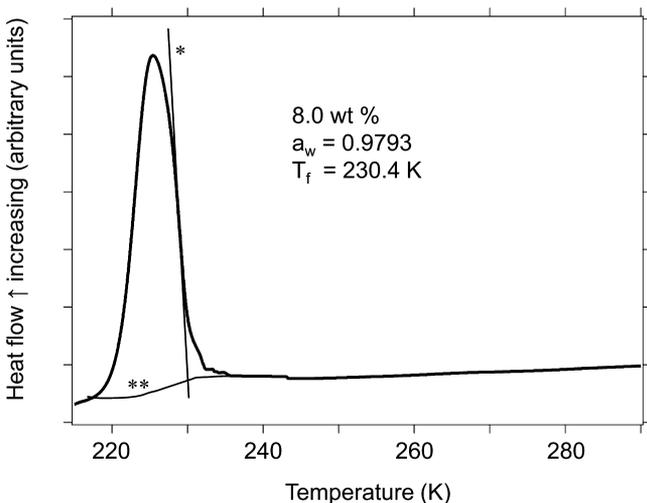
Figure 2. Thermogram of 8.0 wt % ($a_w \sim 0.9793$) aqueous ammonium sulfate particles as temperature is decreased. The line denoted with the star is the tangent line drawn at the inflection of the exothermic peak. The line denoted with the double star is the extrapolated baseline.

was decreased from 290 to 210 K. As the temperature of the sample decreased from 290 K, the baseline of the thermogram remained relatively flat. At approximately 231 K, the particles started to freeze which resulted in an exothermic signal. At approximately 220 K, all of the particles froze and the signal returned to a baseline level. The line denoted with the star in Figure 2 is the tangent line drawn at the inflection of the exothermic peak. The line denoted with the double star is the extrapolated baseline created by the instrument's software

program (sigmoidal baseline). The intersection of the two lines is 230.4 K. This is the T_f for 8.0 wt % ammonium sulfate particles and is denoted with the arrow pointing to the filled circle in Figure 1.

Figure 3 is a thermogram of the ammonium sulfate particles used to generate Figure 2. However, in this thermogram, the

8.0 wt %
a_w = 0.9776
T_m = 271.1 K
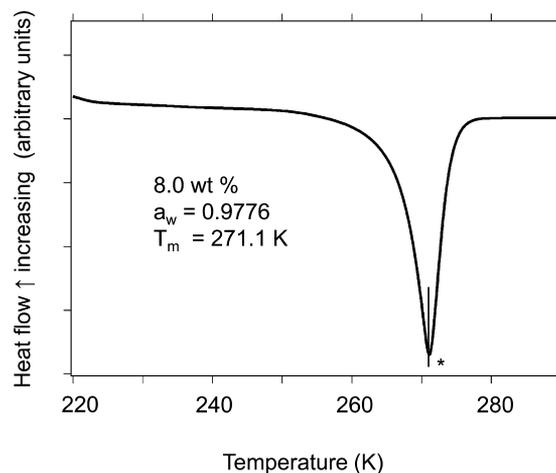
Figure 3. Thermogram of 8.0 wt % ($a_w \sim 0.9776$) aqueous ammonium sulfate particles as temperature is increased. The line denoted with the star is the peak in the endothermic signal.

temperature was raised from 220 to 290 K. As the temperature of the sample increased from 220 K, the baseline of the thermogram remained relatively flat. At approximately 255 K, the particles started to melt which resulted in an endothermic signal. When the sample was warmed to approximately 276 K, the particles all melted and the signal flattened out to a baseline level. The vertical line denoted with the star in Figure 3 is the peak in the endothermic signal determined using the instrument's software program. The peak at 271.1 K is the T_m for the 8.0 wt % aqueous ammonium sulfate particles and is denoted with the arrow pointing to the open circle in Figure 1.

Homogeneous freezing and melting experiments were performed using several different concentrations of aqueous ammonium sulfate particles. The results of the experiments are shown in Figure 1. In theory, when the aerosol particles are pure water ($a_w = 1$), they should freeze at approximately 235 K.[3] This phenomenon can be explained by the fact that the liquid to solid transition in micron-sized aqueous droplets is a kinetic, nonequilibrium process. Four separate freezing experiments were performed with emulsified water droplets to determine if the DSC was operating correctly. An average T_f of 237.3 ± 0.9 K was found. The average T_f is slightly warmer than that predicted for water droplets. However, some of the laboratory experiments presented in Koop et al.[3] found freezing temperatures slightly warmer than 235 K. Therefore, we are confident the DSC was correctly measuring phase transitions in the aerosol particles.

Figure 1 shows the T_f (solid circles) of the particles decrease as the amount of solute increases (a_w decreases). This illustrates the concept of the colligative property of freezing point depression. Additionally, T_f values of all aerosol particles in this study agree (within error) with the Koop et al.[3] model of homogeneous ice nucleation. Figure 1 also shows T_m (open circles) of the ammonium sulfate aerosol particles. As with T_f, T_m values agree well with the Koop et al.[3] model.

CONCLUSION

Homogeneous ice nucleation is an important mechanism for the formation of cirrus clouds. To understand the effect cirrus clouds have on the Earth's radiation budget, it is important to understand the conditions at which they form. Therefore, it is crucial to determine how dissolved solutes affect the freezing and melting temperatures of micrometer-sized aerosol particles. In this laboratory experiment, undergraduate students modeled the freezing and melting temperatures of aqueous aerosol particles using the Koop et al.[3] theory. With this the model, a T_f of approximately 235 K and a T_m of approximately 273 K were calculated for pure water particles $(a_w = 1)$. Additionally the T_f and T_m of the aerosol particles decreased with decreasing a_w. The Koop et al.[3] homogeneous ice nucleation model theoretically illustrates the concept of freezing point depression in conjunction with cirrus cloud formation mechanisms. The undergraduate students used a DSC to experimentally determine the T_f and T_m of aerosol particles containing various amounts of ammonium sulfate. The experiments agreed well with the Koop et al.[3] theory. Therefore, the Koop et al.[3] homogeneous ice nucleation model was verified using a thermal method of analysis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00663.

> Additional information for students and instructors concerning hazards, experimental procedure and a time-line for the completion of the experiments (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) D'Amelia, R.; Franks, T.; Nirode, W. F. Introduction of differential scanning calorimetry in a general chemistry laboratory course: Determination of molar mass by freezing point depression. *J. Chem. Educ.* **2006**, *83* (10), 1537−1540.

(2) Knopf, D. A.; Rigg, Y. J. Homogeneous ice nucleation from aqueous inorganic/organic particles representative of biomass burning: water activity, freezing temperatures, nucleation rates. *J. Phys. Chem. A* **2011**, *115*, 762−773.

(3) Koop, T.; Luo, B. P.; Tsias, A.; Peter, T. Water activity as the determinant for homogeneous ice nucleation in aqueous solutions. *Nature* **2000**, *406* (6796), 611−614.

(4) Andriyevsky, B.; Doll, K.; Jansen, M. First principles study of structural stability, electronic and related properties of $(NH_4)_2SO_4$. *J. Phys. Chem. Solids* **2010**, *71* (3), 357−363.

(5) Zobrist, B.; Marcolli, C.; Koop, T.; Luo, B. P.; Murphy, D. M.; Lohmann, U.; Zardini, A. A.; Kreiger, U. K.; Corti, T.; Cziczo, D. J.; Fueglistaler, S.; Hudson, P. K.; Thomson, D. S.; Peter, T. Oxalic acid as a heterogeneous ice nucleus in the upper troposphere and its indirect aerosol effect. *Atmos. Chem. Phys.* **2006**, *6*, 3115−3129.

(6) Pinti, V.; Marcolli, C.; Zobrist, B.; Hoyle, C. R.; Peter, T. Ice nucleation efficiency of clay minerals in the immersion mode. *Atmos. Chem. Phys.* **2012**, *12* (13), 5859−5878.

(7) Clegg, S. L.; Brimblecombe, P.; Wexler, A. S. A thermodynamic model of the system H^+-NH_4^+-SO_4^{2-}-NO_3^--H_2O at tropospheric temperatures. *J. Phys. Chem. A* **1998**, *102* (12), 2137−2154. See also http://www.aim.env.uea.ac.uk/aim/aim.php (accessed Dec. 2015).

(8) Wendlandt, W. W. *Thermal Analysis*, 3rd ed.; John Wiley: NewYork, 1986.

(9) Marti, J.; Mauersberger, K. A survey and new measurements of ice vapor pressure at temperatures between 170 and 250 K. *Geophys. Res. Lett.* **1993**, *20* (5), 363−366.

(10) Murphy, D. M.; Koop, T. Review of the vapour pressures of ice and supercooled water for atmospheric applications. *Q. J. R. Meteorol. Soc.* **2005**, *131*, 1539−1565.

(11) Koop, T. Homogeneous ice nucleation in water and aqueous solutions. *Z. Phys. Chem.* **2004**, *218* (11), 1231−1258.