

The Effects of Temperature on the Deliquescence of Atmospheric Aerosols

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Abstract — The dependence of the deliquescence relative humidity (DRH) on temperature is investigated for several inorganic salt particles. The vapor pressure of water above a saturated salt solution was measured and used to calculate the DRH of the corresponding salt particle. This was performed at a series of temperatures between 0 and 35°C for NaCl, KCl, (NH₄)₂SO₄, NaNO₃, NaBr, and CsCl. The results are compared with literature values. This is the first study to report systematic measurements of the dependence of DRH on temperature for CsCl, and our data are in agreement with individual literature values for DRH at 6°C and 25°C.

Introduction

Aerosol salt particles, which arise from a variety of natural and anthropogenic sources, play a very important role in the chemistry and dynamics of the atmosphere. While typical aerosols are produced by many different sources (e.g., volcanic eruption, dust storms, sea salt, combustion, and biomass burning [Hinds, 1982]), this paper will focus on sea salt aerosols. Sea salt aerosol particles are the dominant species (by mass) over the world's oceans. While the mechanisms by which they influence climate are known, their effects remain poorly understood [Buseck and Posfai, 1999]. Aerosol particles can directly affect the Earth's climate by absorbing and scattering incoming solar radiation, resulting in an overall cooling effect. Aerosols also affect the global radiative budget indirectly by acting as cloud condensation nuclei and influencing cloud lifetimes [Charlson *et al.*, 1992]. A final important role of aerosols, particularly of sea salt aerosols, is that they serve as a surface for heterogeneous chemistry in the atmosphere [Buseck and Posfai, 1999]. Understanding the life cycle of aerosol particles is very important to evaluating the effects of these processes and their ultimate impact on global climate.

An important distinction among inorganic aerosol particles is whether they are in the crystalline (solid particle) or aqueous (droplet) phase. At low values of relative humidity (RH) inorganic aerosols exist as small crystalline particles. As the amount of water vapor in the air increases, they remain in the solid phase up to a threshold value of RH known as the deliquescence relative humidity (DRH). At the DRH, water vapor condenses on the solid particle in a process known as deliquescence to form a saturated aqueous droplet. If RH increases further, water will continue to condense on the droplet, causing it to grow in size in order to maintain equilibrium with the surrounding water vapor. This phenomenon is driven by free energy; deliquescence occurs when the free energy corresponding to the crystal and the droplet are equal, with the crystalline phase having a lower free energy at lower values of RH and the aqueous droplet having lower free energy at higher values of RH [Seinfeld and Pandis, 1998].

A good understanding of deliquescence is important because the crystalline and aqueous phases have very different properties and very different effects on climate. One important difference in the activity of these phases is in the scattering of radiation. Solution droplets are considerably larger in size than crystalline particles, and therefore scatter visible wavelength light considerably more efficiently [Martin, 2000]. Because of

these differences, it is important to have a good understanding of which phase is more favorable in the atmosphere under given conditions in order to evaluate the role of aerosols in climate forcing.

An important part a full understanding of deliquescence is how DRH is affected by changes in temperature. Temperature affects the vapor pressure of the droplet, changing the point at which equilibrium is established with the surrounding water vapor, and thus changing the DRH of certain salts. As temperature increases, the vapor pressure of a droplet of a given concentration increases, allowing a stable droplet to exist at higher salt concentrations and thus lower water concentrations and lower RH values. DRH therefore tends to decrease as temperature increases, with the scale of the effect varying for each individual salt [Seinfeld and Pandis, 1998].

The relationship between DRH and temperature has been studied both theoretically and experimentally. Greenspan (1977) compiled DRH vs. temperature data from 21 separate investigations for a variety of salts, weighing each investigation based on the estimated uncertainty of the method. Tang and Munkelwitz (1993) studied the relationship between DRH and temperature using both theoretical calculations and experiment. Their experiments involved measuring the DRH of charged particles suspended in an electrodynamic cell. Apelblat (1993) measured the relationship between the vapor pressure of water above a saturated solution and temperature using an evaporimeter. However, studies of the effects of temperature on DRH are far from complete. The relationship is different for each salt, and has not been established for many atmospherically relevant particles.

In addition, Wise *et al.* (2005) measured the DRH of several salts using an environmental transmission electron microscope (ETEM). Due to the constraints of the microscope, the data were collected at 6°C. This made comparison of the results to the literature difficult because DRH is typically studied near 25°C. In addition to our other stated goals, this paper seeks to corroborate the data of Wise *et al.*, particularly for cesium chloride, for which no data exist in the literature at 6°C.

In this study, we determined the DRH of single salt aerosols by measuring the vapor pressure of water over a saturated salt solution. This is a viable model for studying deliquescence for two main reasons. First, when a crystal deliquesces it forms a saturated solution droplet that is in equilibrium with the surrounding water vapor. It is therefore possible to determine the DRH by simply measuring the vapor pressure of water in equilibrium above a saturated salt solution, without accounting for the solid phase or the phase transition itself. Secondly, for droplets greater than 100 nm in diameter, surface contributions to the free energy (Kelvin effect) are negligible compared to the free energy of the droplet itself. The vapor pressure associated with a curved droplet is therefore the same as that associated with a flat surface solution [Seinfeld and Pandis, 1998]. Taking advantage of these principles, we were able to measure the DRH associated with single salt aerosols larger than 100 nm by measuring the vapor pressure of water over a large-scale saturated solution. This is particularly significant because micron-sized particles, which are modeled well by our study, are responsible for most of the scattering of radiation in the atmosphere.

In this paper, we measure the dependence of DRH on temperature for NaCl, KCl, (NH₄)₂SO₄, NaNO₃, NaBr, and CsCl. Our findings supplement existing DRH data and

provide new information for cesium chloride, which has never previously been characterized in this way.

Experimental

The experimental setup that was used to measure the DRH at a range of temperatures is shown in Figure 1. The salts used were high purity and used as purchased (NaCl, KCl, NaNO₃, Mallinckrodt Chemicals 100.0% pure; (NH₄)₂SO₄, NaBr, EMD Chemicals, 99.0% pure; CsCl, Shelton Scientific, 99.9% pure). Distilled deionized water was used for all solutions. A saturated salt solution was placed in a round-bottom flask which was immersed in a constant temperature bath. Solid salt was left in the solution to ensure saturation at all times. The upper part of the flask was connected to a vacuum

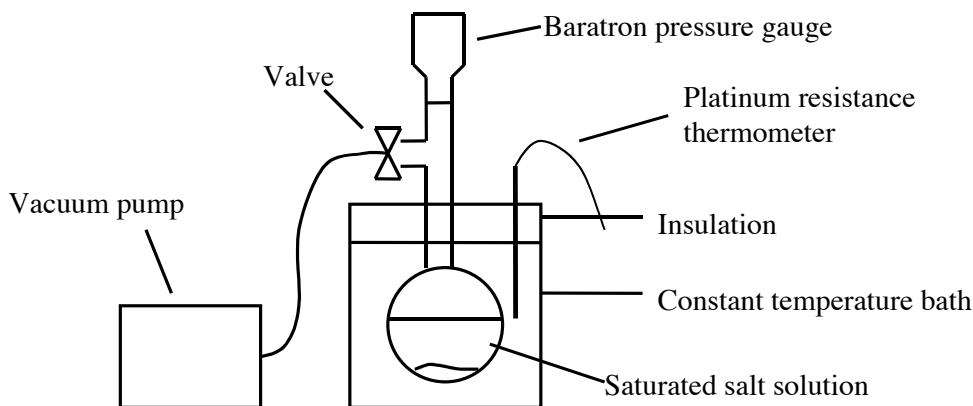


Figure 1: Experimental Setup

pump and a pressure gauge in a closed system. The vacuum pump was used to remove all air from above the solution, so that the pressure given by the pressure gauge after the pump was switched off and the system allowed to equilibrate was that of water vapor alone. The DRH corresponding to salt under consideration could then be calculated for the equilibrium system according to:

$$\text{DRH} = \frac{P_{\text{sol}}(T)}{P_{\text{H}_2\text{O}}(T)} \times 100, \quad (1)$$

where P_{sol} is the vapor pressure of water above the solution at temperature T and $P_{\text{H}_2\text{O}}$ is the vapor pressure of pure water at temperature T .

In a typical experiment, the system was opened to the vacuum pump for approximately 5 seconds and the valve was then shut for 5–10 minutes. This procedure was repeated several times to allow for the removal of any air dissolved in the solution, ensuring that the vapor pressure measured by the pressure gauge corresponded to water vapor alone. The system was then allowed to equilibrate at a given temperature for approximately 20 min before the temperature and pressure of the system were recorded. The temperature of the system was recorded with a platinum resistance thermometer and the pressure with a Baratron pressure gauge. Before each measurement, the system was briefly opened to the vacuum to remove any air that had effervesced from the solution or leaked in from the outside, and the system was allowed to equilibrate. This process was

repeated for a range of temperatures between 0 and 35°C for each salt. Data were obtained for both heating and cooling of the solution to assure that this did not affect results. The pressure was monitored carefully to make sure that there were no leaks of outside air into the system. If a leak was suspected, the system was closed with an empty flask and brought to a tight vacuum. The pressure was then monitored to determine how quickly air leaked into the system. Measurements were not taken unless the system showed less than 0.2 torr increase in pressure from vacuum over 10 minutes.

No more than four data points were obtained for a given solution before the apparatus was cleaned and dried to remove any water droplets that had condensed in the connectors. Condensation affected pressure readings because the vapor pressure associated with a pure water droplet is greater than that associated with the salt solution. The formation of droplets was most common above room temperature, when the upper part of the apparatus was at a lower temperature than the solution in the bath. To alleviate this problem, heating tape was placed around the upper part of the apparatus for points above room temperature and set to the same temperature as the bath. This was successful up to 35°C, but at higher temperatures there were still large fluctuations in pressure, limiting collection of useful data above 35°C.

Results and Discussion

To demonstrate the viability of the method, the dependence of DRH on temperature was first studied with salts for which data are available in the literature: sodium chloride, potassium chloride, ammonium sulfate, sodium nitrate, and sodium bromide. The data obtained for these salts are shown in Figures 2–6 and in Table 1 (see Appendix). Figures 2–6 show DRH as a function of temperature and illustrate the comparison between this study and the literature data. For NaCl, KCl, and NaNO₃, the data are in good agreement with all literature values. (NH₄)₂SO₄ data show good agreement with Tang and Munkelwitz (1993), but consistently disagree by approximately 2% with the study by Greenspan (1977). However, this is not discouraging because Tang's method using an electrodynamic cell is likely more accurate than the methods compiled by Greenspan from before 1977. There is no agreement among our data, that of Greenspan (1977), and that of Apelblat (1993) for NaBr. More data should be taken for this salt to obtain a better understanding of where the error lies. Overall, the trends shown by our data for these salts are in good agreement with the literature, demonstrating that the method used in this paper is viable for studying the relationship between DRH and temperature. Our results for these salts also provide additional information to aid in the standardization of DRH vs. temperature data.

Once the accuracy of our method was established, we were able to determine the dependence of DRH on temperature for cesium chloride, for which this relationship has never been studied. The results obtained for CsCl are shown in Figure 7 and Table 2 (see Appendix). We determined a fairly strong dependence of DRH on temperature, with DRH decreasing 4.5% over 35°C. In addition, our data were in agreement with the DRH determined at 25°C by Richardson and Snyder (1994) and the DRH determined at 6°C by Wise *et al.* (2005).

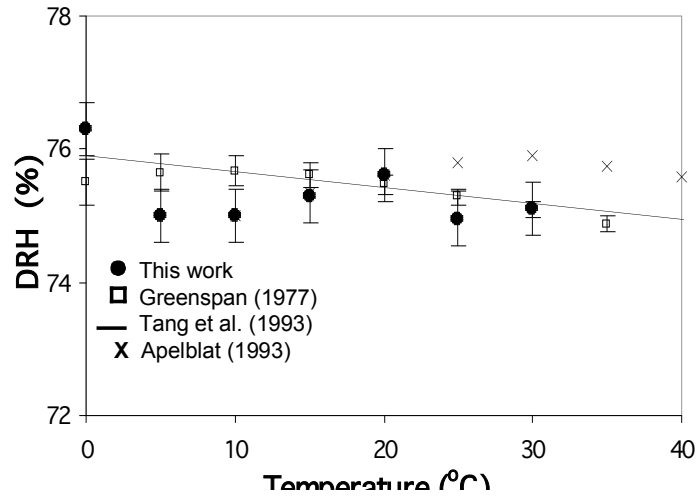


Figure 2: Deliquescence relative humidity of NaCl as a function of temperature.

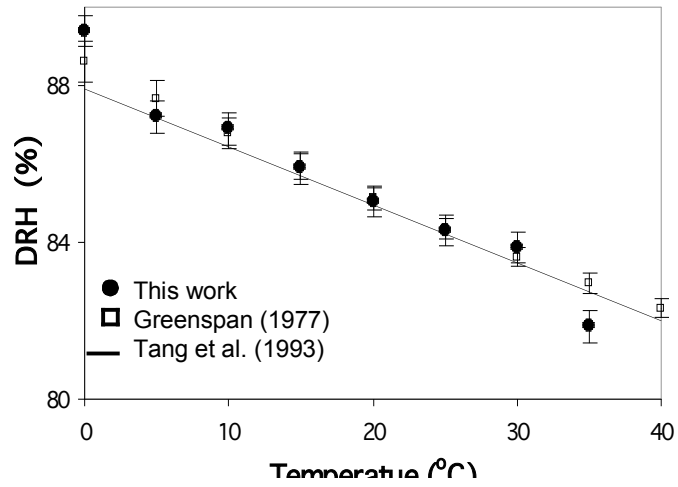


Figure 3: Deliquescence relative humidity of KCl as a function of temperature.

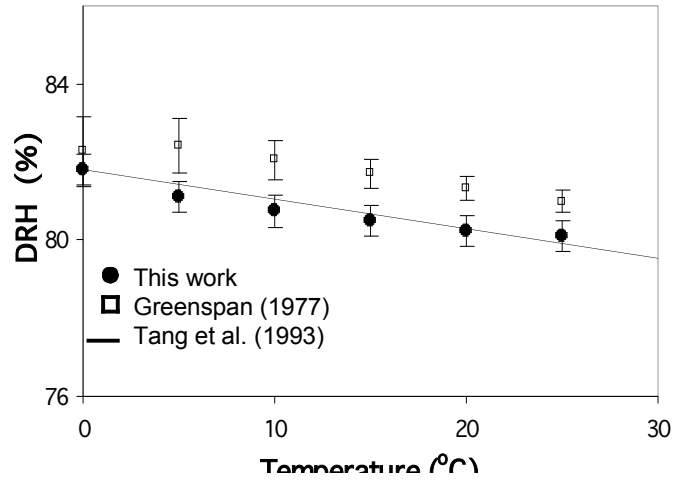


Figure 4: Deliquescence relative humidity of $(\text{NH}_4)_2\text{SO}_4$ as a function of temperature.

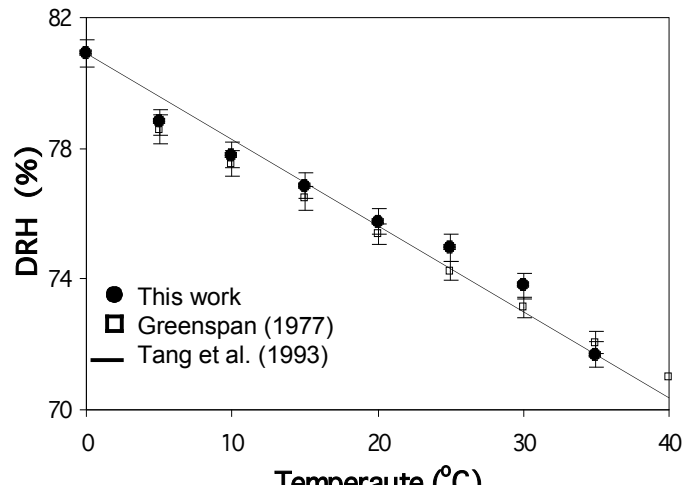


Figure 5: Deliquescence relative humidity of NaNO_3 as a function of temperature.

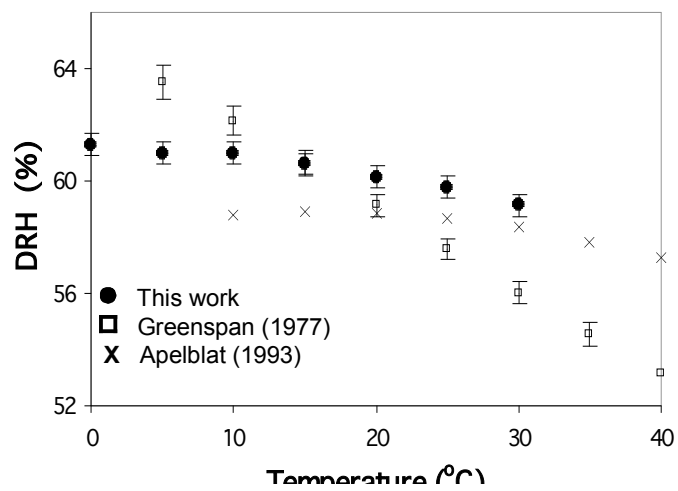


Figure 6: Deliquescence relative humidity of NaBr as a function of temperature.

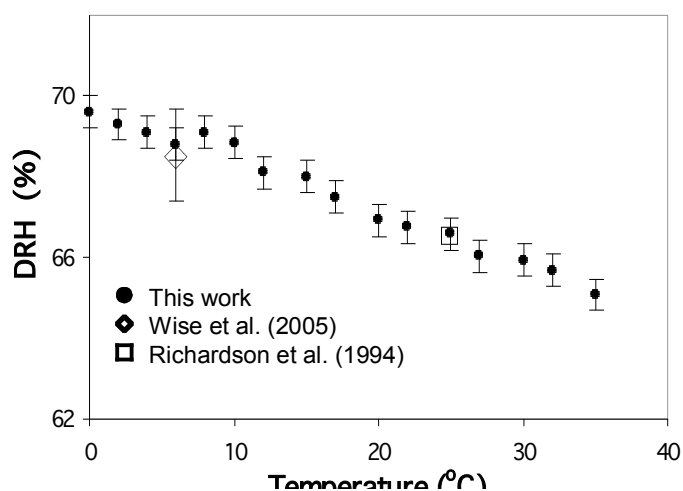


Figure 7: Deliquescence relative humidity of CsCl as a function of temperature.

Conclusions

The dependence of the deliquescence relative humidity of several salts on temperature has been determined over the range of 0 to 35°C. The DRH was calculated from temperature and vapor pressure measurements above a saturated solution of the salt under consideration. Data for NaCl, KCl, (NH₄)₂SO₄, and NaNO₃ are in good agreement with most literature values, demonstrating the viability of our method. These data also aid in the standardization of DRH vs. temperature curves. The dependence of DRH on temperature was measured for CsCl and the results showed good agreement with individual literature values at 6°C and 25°C. These results supplement the existing data for the DRH of CsCl at different temperatures and provide the first complete data set in the temperature range of 0 to 35°C.

Appendix

Table 1: Deliquescence relative humidity as a function of temperature for single salt aerosols

Temperature (°C)	NaCl	KCl	(NH ₄) ₂ SO ₄	NaNO ₃	NaBr
0	76.4	89.5	81.9	81	61.3
5	75.1	87.3	81.2	78.9	61.0
10	75.0	86.9	80.67	77.85	61.0
15	75.30	85.90	80.69	77.20	60.60
20	75.60	85.06	80.30	75.77	60.13
25	75.00	84.34	80.10	74.66	59.77
30	75.22	83.99		73.90	59.14
35		81.85		71.69	

Table 2: Deliquescence relative humidity as a function of temperature for cesium chloride

Temperature (°C)	DRH%
0	69.6
2	69.3
4	69.1
6	68.8
8	69.1
10	68.8
12	68.1
15	67.9
17	67.5
20	66.93
22	66.76
25	66.58
27	66.03
30	65.94
32	65.68
35	65.08

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