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LIQUID TO LIQUID AND CRITICAL NUCLEUS TO CRITICAL NUCLEUS PHASE TRANSITIONS IN SUPER-COOLED DROPLETS

D. Imre, R. McGraw, J. Xu, and S. Oatis
Environmental Chemistry Division
Department of Applied Science
Brookhaven National Laboratory
Upton, NY 11973

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Dan Imre, Robert McGraw, Jun Xu, and Susan Oatis

Environmental Chemistry Division, Brookhaven National Laboratory
Upton, NY 11973

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I. LIQUID-LIQUID PHASE TRANSITIONS: A new low-temperature single-particle levitation cell was used to study the properties of super-cooled/super-saturated electrolyte solutions of ammonium sulfate and ammonium bisulfate aerosols. The observations indicate an abrupt change in the colligative properties of these metastable water solutions near 5°C. The data suggest the existence of high and low temperature states each behaving in a simple predictable manner, yet surprisingly different from each other. These observations are consistent with a liquid-liquid structural phase transition during which a fraction of the water molecules changes its role from the solvent to the solute by tightly binding to the ammonium sulfate ions. This phase transition starts at 15°C and is complete at –5°C. In the case of ammonium sulfate the solute, in the low temperature state is a tetrahydrate form of ammonium sulfate. This phase is consistent with our newly discovered, stable, low temperature tetrahydrate crystalline phase of ammonium sulfate.

The super-cooled and super-saturated ammonium bisulfate water solution contains ~6 waters per solute molecule. The thermodynamic data indicate that 4 of these waters are tightly bound to the solute. At the same low temperatures, but higher RH where the solution is dilute, the solute transforms to an octahydrate phase, which is also the stable crystalline phase of this system at low temperatures.

Through all of the above transformations the solution droplets remain homogeneous. The fact that the transition between the low and high temperature states is centered near 4 °C suggests that it might be a manifestation of the property of water and could therefore be universal property of aqueous media.

II. HOMOGENEOUS NUCLEATION: We will present results of experiments in which the dynamics of homogeneous liquid-to-solid nucleation in super-cooled/saturated single isolated microparticles have been studied over a wide range of temperatures.

Results for ammonium sulfate, and ammonium bisulfate water solutions will be presented. On the basis of these data we derived detailed information on the properties of the critical nuclei in these systems. For example, we find for ammonium sulfate that at 25 °C the critical nucleus is composed of 40 ammonium sulfate molecules and 28 at 5 °C. We derived nucleus enthalpy, entropy, surface tension etc. At temperatures below 5°C where the metastable solution undergoes a liquid-liquid transition the data indicate that the critical nucleus is also transforming from anhydrous to ammonium sulfate tetrahydrate as shown in Figure 1 below.

III. HETEROGENEOUS NUCLEATION: In this set of experiments we introduced a crystalline impurity into an ammonium sulfate solution droplet in order to study its effect on the nucleation process. We find that a $CaCO_3$ impurity 250nm in diameter provides a nucleation site critical super-saturation ratio from 2.16 for the homogeneous case to 1.65. When the heterogeneous nucleus is reduced to 25nm in diameter this number is increased to 1.86. The ammonium sulfate critical nucleus that forms on the 250nm $CaCO_3$ impurity is composed of 20 molecules. Scaling expressions for the heterogeneous nucleation rate will be described.

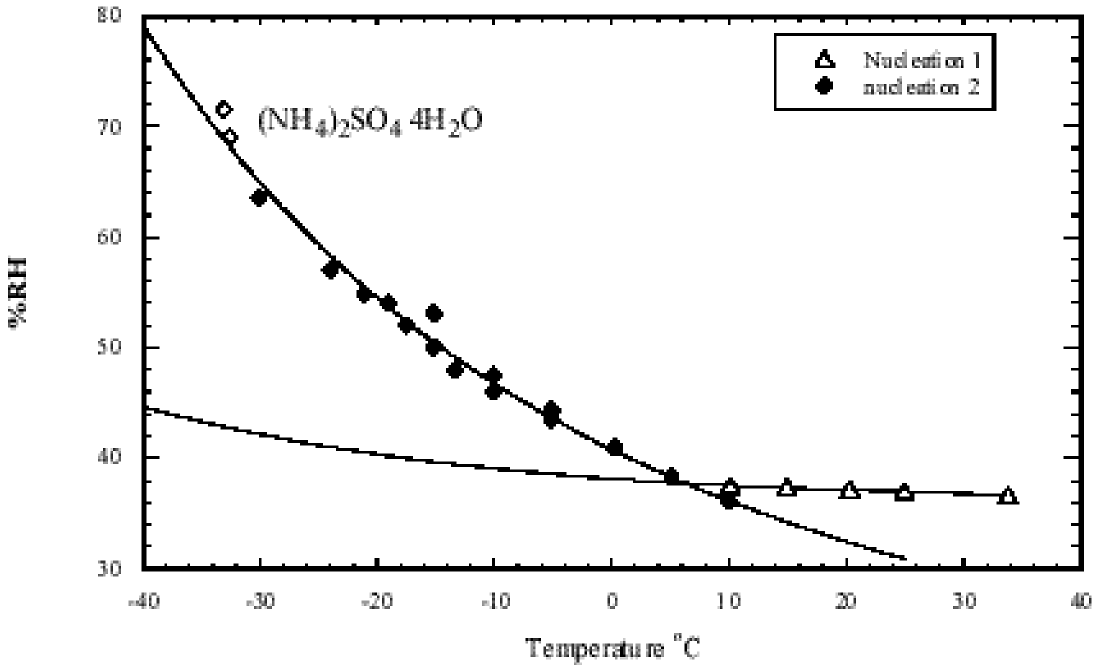

Figure 1. A plot of the observed nucleation conditions in RH vs. Temperature for ammonium sulfate/water suspended droplets. The open triangles are the nucleation events where the critical nucleus is anhydrous. The diamonds are the efflorescence points where the tetrahydrate is the critical nucleus. In all cases except for the two data points labeled with open diamonds the final crystal is anhydrous.