A perspective on the influence that biomass burning may have on cirrus clouds: Freezing of solutions catalyzed by high molecular weight organic compounds

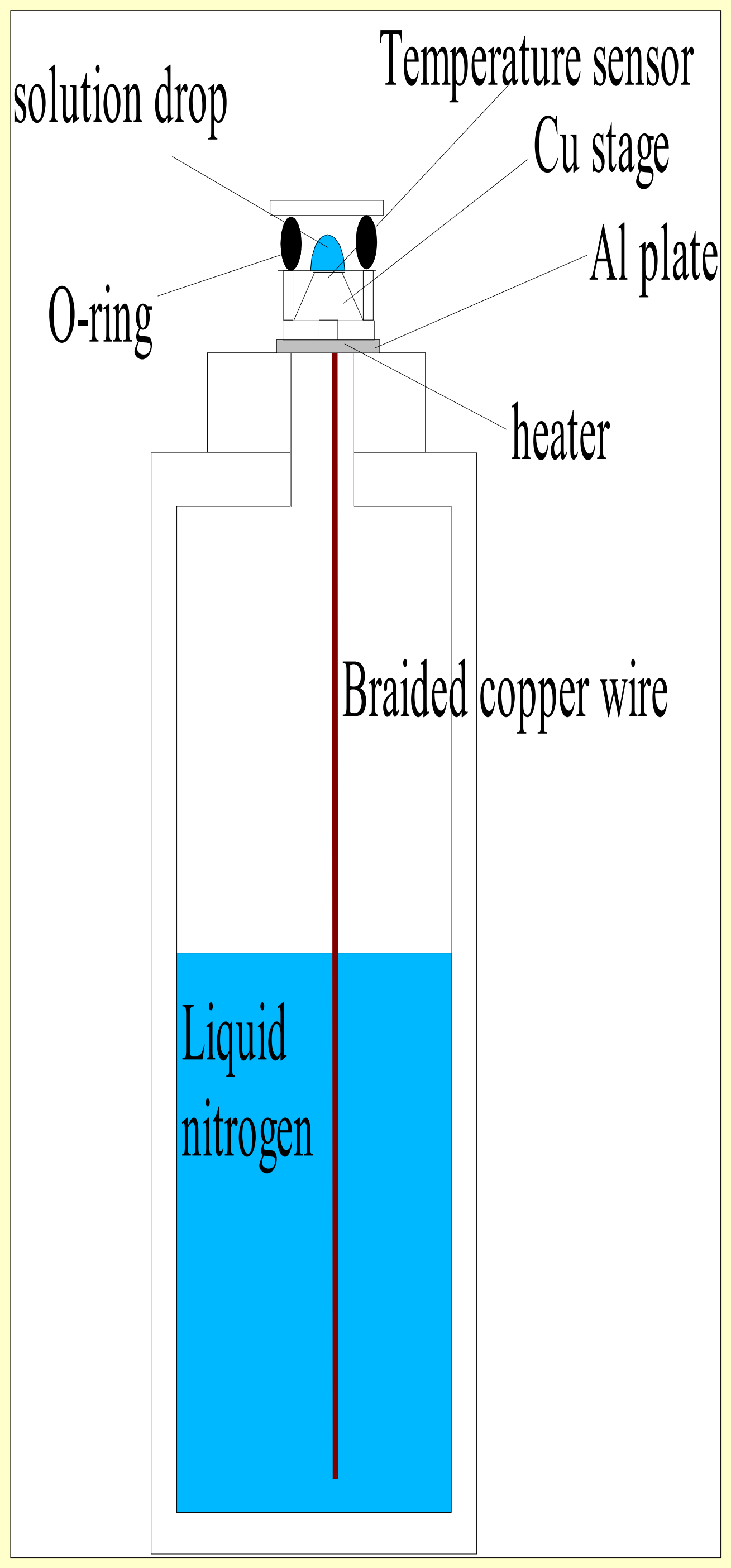
Carly Robinson and Will Cantrell
Dept. of Physics, Michigan Technological University

Abstract

Deep convection frequently carries the products of biomass burning into the upper troposphere. A better understanding of this phenomenon would shed light on how the products of the burning are affecting the properties of cirrus clouds. Ice nucleation mechanisms are thought to be the most important property that is being affected by the burning. In biomass burning, aerosol particles are most likely a mixture of organic compounds and salts. We have investigated freezing events of sodium chloride and ammonium sulfate solutions. Freezing is catalyzed by pentacosanol ($C_{25}H_{51}OH$). Because of its high molecular weight, pentacosanol is insoluble in water; it self-assembles into a two-dimensional crystal at the air-water interface.

Our results indicate that heterogeneous nucleation from a solution, catalyzed by pentacosanol follows Koop et al.'s (2000) supposition that nucleation is a function only of the water activity.

Technical Details

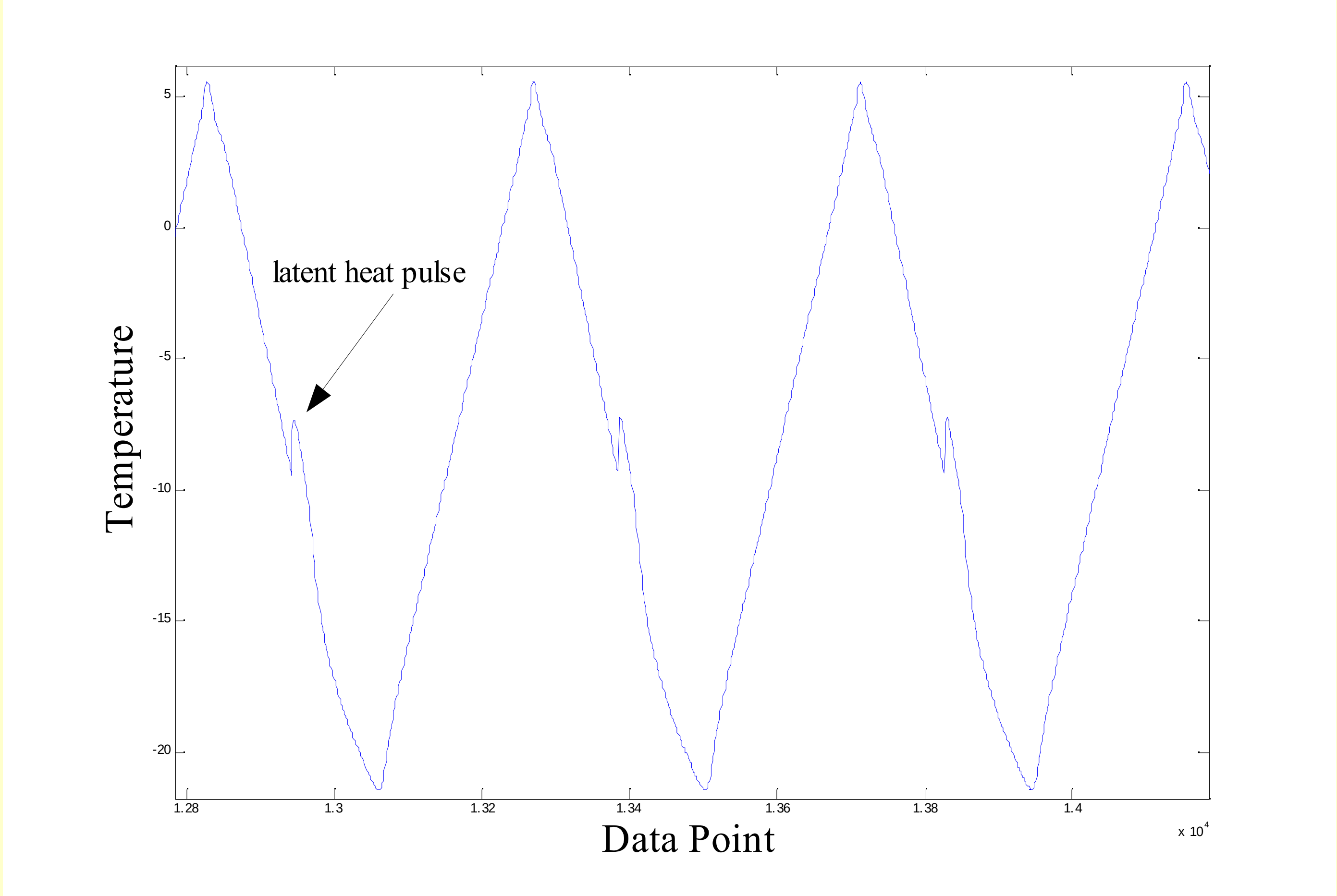


- A 10µl drop of solution is placed on a glass slide, which sits upon the copper stage. 10µl of an alcohol-chloroform solution is put on the droplet. The chloroform evaporates leaving a two-dimensional crystal of the alcohol on the droplet.

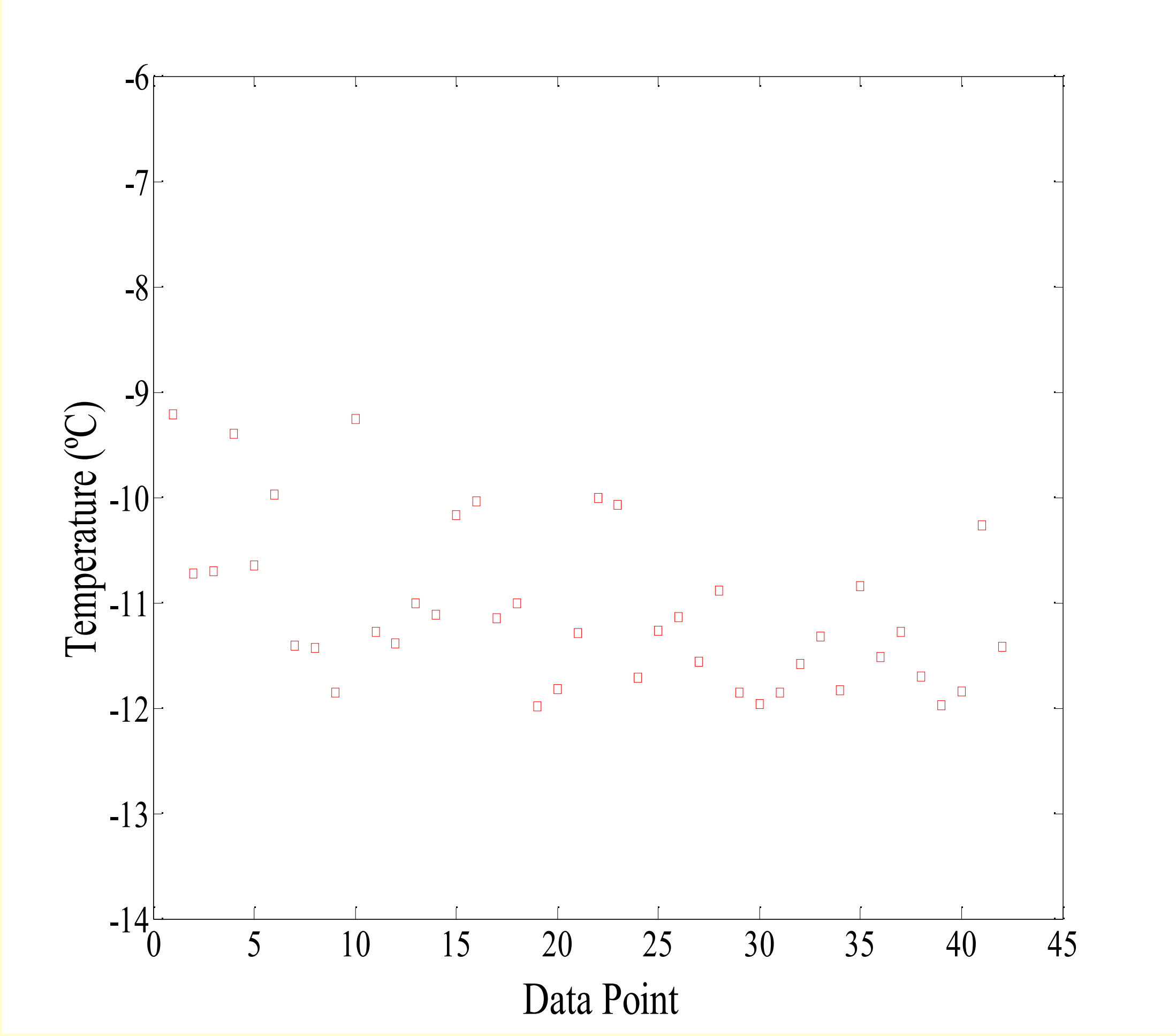
- Temperature is controlled with a Lakeshore Model 331 T controller. A resistive heater provides the heat necessary to raise the temperature of the system above that of the LN2 reservoir.

- Temperature is measured with a thin-film resistance thermal device (rtd), which has a negligible heat capacity. It is sandwiched between the copper stage and glass slide. (The thermal resistance of the glass slide is negligible as well.)

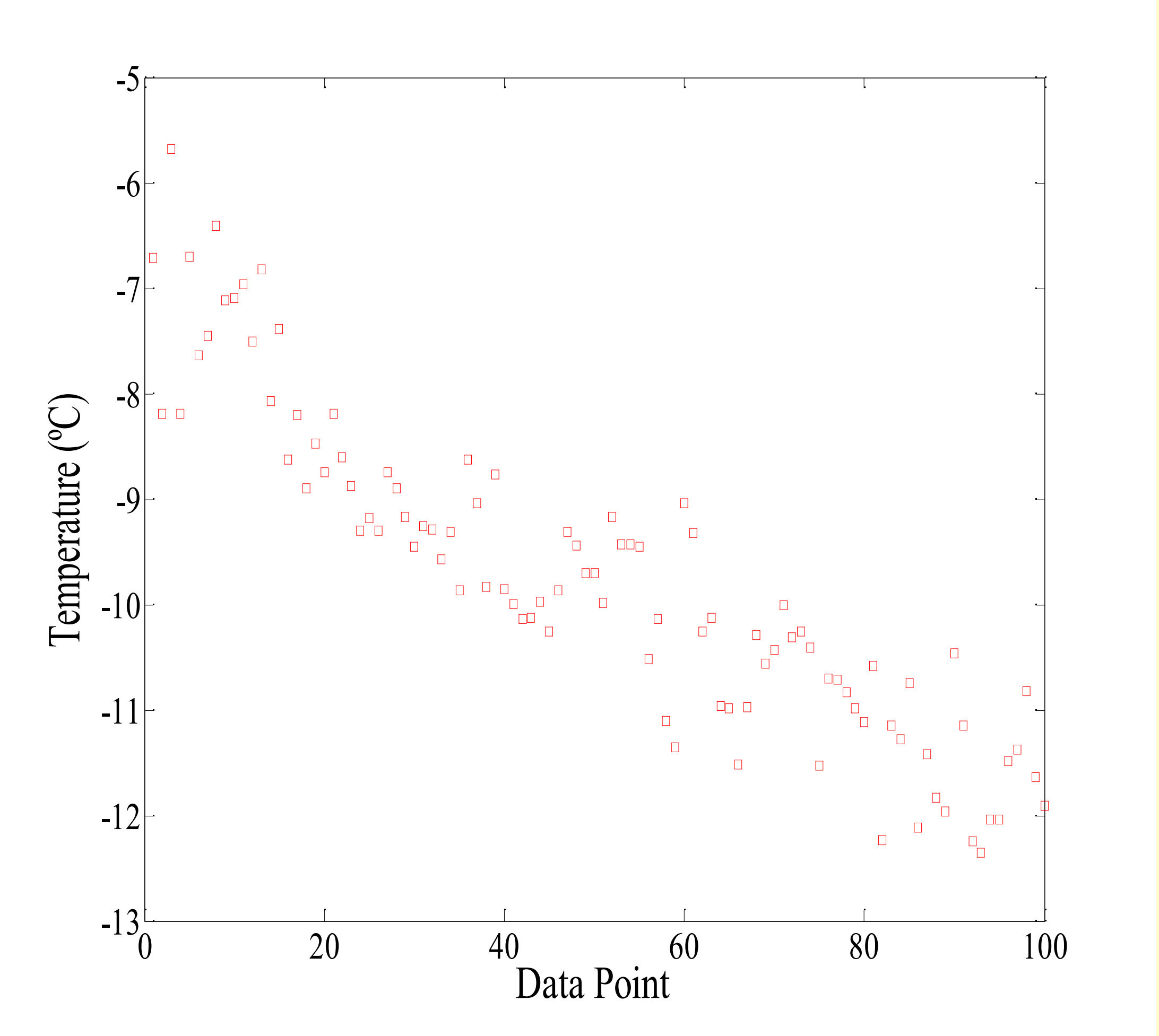
- The latent heat pulse given off by the droplet temporarily disrupts the programmed temperature decrease. The freezing point we record is the point at which the temperature starts to rise.



An example of the raw data.
$|dT/dt| = 3$ K/min.



The freezing point as a function of trial number for a 0.75 molar solution of ammonium sulfate.

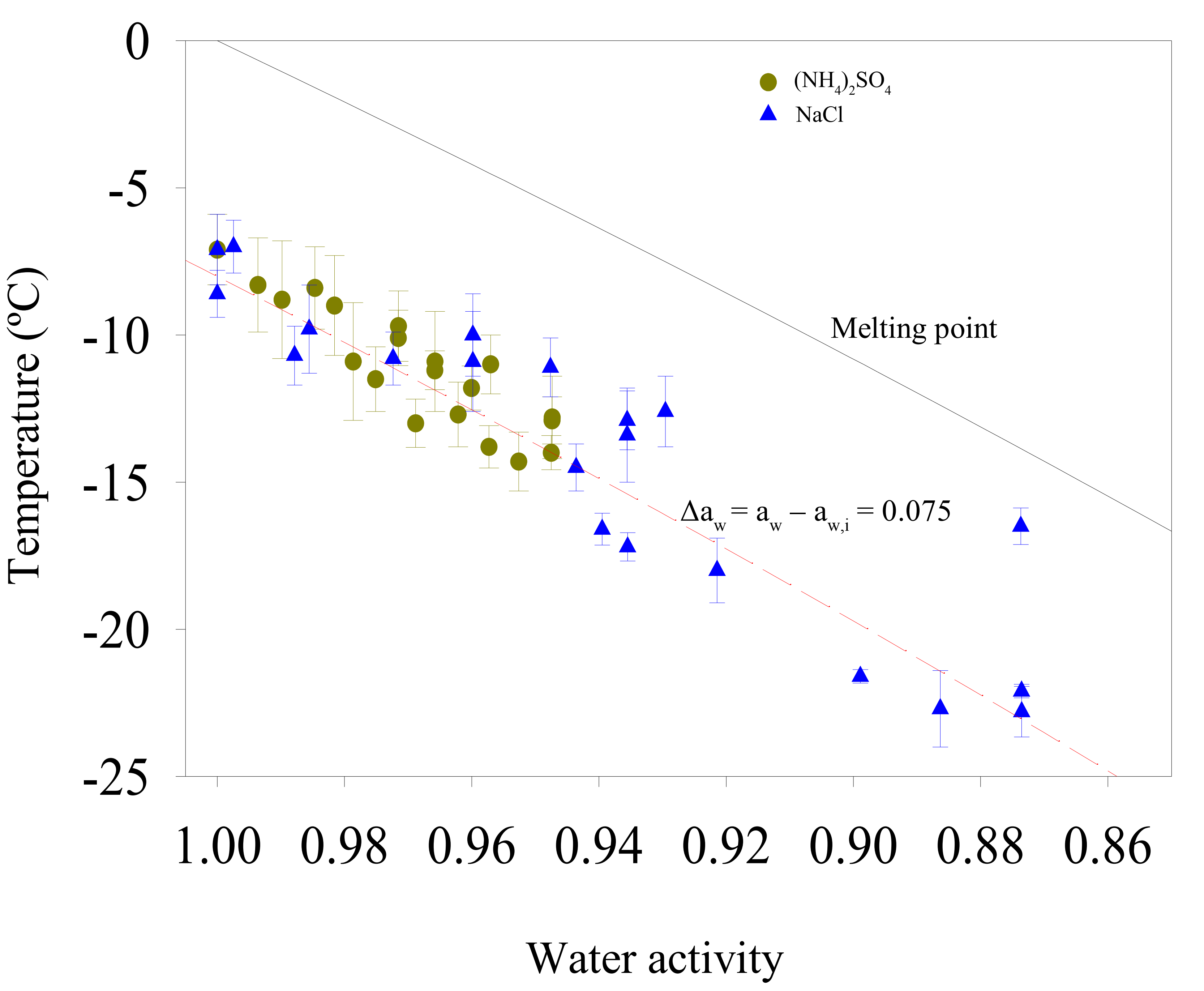


In many cases we find that the freezing temperature decreases as a function of time.

Possible explanations for the decrease in freezing temperature with time

- Water is evaporating, resulting in a more concentrated solution. Unlikely, since size of droplet appears unchanged over the course of the experiment.
- The alcohol is evaporating. Unlikely, since the alcohol is not volatile. It is a solid at room temperature.
- The alcohol is dissolving into the solution. Unlikely. The alcohol is essentially insoluble in water
- Is the alcohol monolayer being disrupted by the repeated freeze-thaw cycles?

Freezing of solutions catalyzed by ($C_{25}H_{51}OH$) as a function of water activity



Temperature dependent water activities for ammonium sulfate solutions were calculated from the known molarity of the solution and the freezing temperature using the formalism in Clegg et al. (1995). The water activities for the sodium chloride solutions are calculated from Clegg et al. (1998), which is for T = 298.15. Water activity in solution is not a strong function of temperature, so we have not attempted to account for the temperature dependence in the NaCl solutions.

Koop et al. (2000) have hypothesized that freezing can be predicted on the basis of water activity alone. Their initial formulation was for homogeneous nucleation (i.e. no catalyst), but the notion has been extended to heterogeneous nucleation as well (see e.g. Zuberi et al (2002)).

$\Delta a_w = a_w - a_{w,i}$ where $a_{w,i}$ is the activity of the solution in equilibrium with ice. (The solution is in equilibrium with ice at the melting point, by definition.)

Homogeneous nucleation occurs at $\Delta a_w = 0.305$. Heterogeneous nucleation is hypothesized to follow Δa_w = constant as well.

Our results show that freezing catalyzed by pentacosanol from either ammonium sulfate or sodium chloride solutions is characterized by $\Delta a_w = 0.075$, shown by the dashed red line in the figure to the left.

References:

Clegg S.L., P. Brimblecombe, A.S. Wexler, Thermodynamic model of the system H+-NH4+-Na+-SO42—NB3--Cl--H2O at 298.15 K, *J. Phys. Chem A*, **102**(12), 2155-2171, 1998.
Clegg, S.L., S.S. Ho, C.K. Chan, and P. Brimblecombe, Thermodynamic properties of aqueous $(NH_4)_2SO_4$ to high supersaturation as a function of temperature. *J. Chem. Eng. Data*, **40**, 1079-1090, 1995.
Koop, T., B. Luo, A. Tsias, and T. Peter, Water activity as the determinant for homogeneous ice nucleation in aqueous solutions. *Nature*, **406**, 611-614, 2000.
Zuberi, B., A. Bertram, C. Cassa, L. Molina, and M. Molina, Heterogeneous nucleation of ice in $(NH_4)_2SO_4$-H_2O particles with mineral dust immersions. *Geophys. Res. Lett.*, **29**(10), 10.1029/2001GL014289, 2002.

Acknowledgments:
Funding from the Michigan Tech Research Excellence Fund, NASA, and the National Science Foundation (CHE-0410007) is appreciated.