The Effect of Chemical Additives on Ice-Spike Formation

Samuel Lederer

under the direction of
Dr. Kenneth Libbrecht
California Institute of Technology

Abstract

Solutions of sodium bicarbonate, calcium chloride, ethanol, acetic acid, and methanol, in concentrations ranging from 10^{-7} to 0.1 molar, were frozen under controlled conditions to measure the dependence of ice-spike formation on chemical impurities in water. The probability of ice-spike formation was plotted against molarity of solution to determine general trends for different solutes. The varying effects of different solutes at the same concentrations suggested that freezing-point depression was unlikely to cause inhibition of ice-spike formation in solutions, and a model based on dendritic sheet formation was proposed.

1 Introduction

Ice spikes, or spicules, are thin, tapered projections of ice occasionally formed during the freezing of standing water, sleet pellets [3], and icicles [11]. They are also found when distilled water is frozen in ordinary household ice-cube trays (Figure 1). This phenomenon has been observed and recorded for nearly a century [5], but its causes remain poorly understood.

A qualitative model of the phenomenon was put forth independently by Bally and Dorsey in the early 20th century and remains the most widely accepted description of this effect [2, 3, 5, 14]. For the case of water confined to a container, the model outlines the following sequence (Figure 2). Surface water nucleates around irregularities where it meets the container wall and freezes inward, eventually leaving a small hole in the surface. Meanwhile, water adjacent to the walls of the container begins to freeze, and the temperature of water in the center of the cube falls

Figure 1: Examples of typical ice spikes from water frozen in standard household trays. The spike protrudes from the surface at an angle and tapers from base to tip. Sources: Morris, Libbrecht [15, 13].
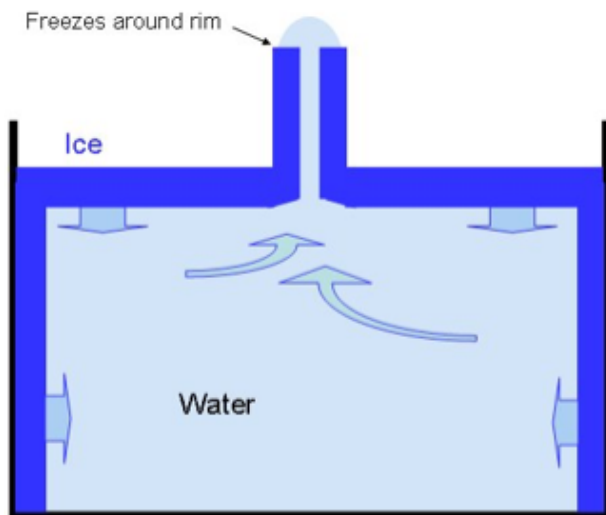
Figure 2: A depiction of the Bally-Dorsey model. Water freezing on the sides of the cube pushes liquid water up through the hole in the surface, where it forms a drop whose freezing edges create the ice spike. Source: Libbrecht, Lui [14].
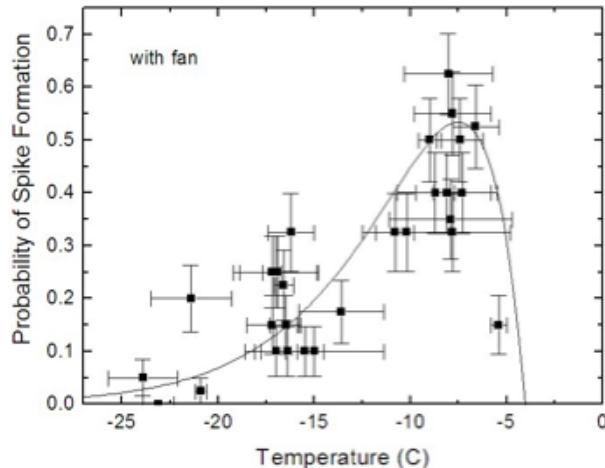

Figure 3: The probability of ice-spike formation versus temperature for pure distilled water in ordinary plastic ice-cube trays. A fan inside the freezing chamber promoted evaporative cooling and facilitated the growth of ice spikes. Probability of ice-spike formation is maximized near $-7°$C. Source: Libbrecht, Lui [14].

below 4°C, causing it to expand. The expansion of interior water and the reduction of volume in the interior of the cube increase the pressure on the water, pushing it upward through the hole. This results in the formation of a drop of water immediately above the hole. The water at the edges of this drop freezes, initiating the tube. As volume within the cube is increasingly taken up by ice, the remaining liquid water is pushed up through this tube and freezes, lengthening the tube. The growth of the tube ceases when the drop at the top of the tube freezes entirely, which is substantially before the rest of the water in the cube is frozen.

Previous research has shown that the formation of ice spikes in pure distilled water is maximized when the water is frozen in ordinary plastic ice-cube trays at a temperature near $-7°$C in the presence of adequate air circulation (Figure 3) [14]. Other reports find that the probability of ice-spike formation is drastically reduced by the presence of impurities in the water [11, 13, 14], an effect which is not addressed in the Bally-Dorsey model. In particular, although ice spikes form readily in most home freezers when distilled water is used, they rarely form from tap water. It is possible that this is due to the colligative

property of freezing-point depression:

$$\Delta T_f = \frac{-1.86\,\text{kg}\cdot{}^\circ\text{C}}{\text{mol}}\cdot mi, \tag{1}$$

where ΔT_f is the change in freezing point; m is the molality of the given solution; and i is the van't Hoff factor, which describes the dissociation of the solute into component ions. For ethanol, methanol, sodium bicarbonate, and calcium chloride, the i factors are 1, 1, 2, and 3, respectively. For acetic acid, the value of i varies as the inverse square root of concentration, with values between 1 and 2 in this experiment. Note that for low concentrations, such as those involved in this experiment, which were less than or equal to 0.1 molar, molality is numerically equivalent to molarity, so these measures will be used interchangeably in calculations.

Eighty percent of tap-water systems in the United States use groundwater [7], and the maximum levels of chemical impurities mandated by the EPA are negligible in comparison to dissolved minerals [8], so a calculation of the freezing-point depression in groundwater may be used to estimate the freezing-point depression in tap water. A common measure of the presence of these mineral impurities in water is total dissolved solids (TDS), expressed in mg/L.

The EPA advises, but does not require, that TDS not exceed 500 mg/L [6]. Estimating TDS as 1000 mg/L, the approximate concentration of impurities in the water may be obtained by consulting Table 1. The total molality of groundwater is approximately 0.002 mol/kg, which would produce a freezing-point depression of only 0.004°C, yet ice spikes are extremely rare in tap water. However, there are also some reports of regular ice-spike formation in tap water. These facts strongly suggest that factors other than freezing-point depression are involved. The purpose of this research is to investigate which chemical impurities facilitate or hinder ice-spike growth and to determine the variation of probability of ice-spike formation as a function of chemical-impurity concentration.

Component	% TDS
Silica (SiO_2)	3.0
Calcium	11.2
Sodium	10.0
Magnesium	2.5
Bicarbonate (HCO_3^-)	62.5
Sulfate (SO_4^{2-})	10.0
Chloride (Cl^-)	5.0

Table 1: Relative concentrations of impurities in groundwater, measured by percentage of total dissolved solids. Source: Ozsvath [16].

2   Materials and Methods

The freezer for this experiment was an insulated copper cylinder cooled by circulating chilled methanol through copper tubing attached to its top and sides. The air temperature within the freezer was maintained near −9°C, and a small electric fan was mounted inside to promote evaporative cooling. Household plastic ice-cube trays were cut to fit inside the tank and, when filled, were positioned on a wire rack approximately 25 cm above the bottom of the tank. Solutions frozen consisted of sodium bicarbonate, ethanol, calcium chloride, acetic acid, and methanol dissolved in laboratory deionized water. Only one solute was present in each trial. Concentrations tested ranged from 10^{-7} to 10^{-1} molar. For each of the trials, 5 trays, each containing 10 cubes, were filled with the appropriate solution, placed in the freezer for approximately 6 hours, and then removed and inspected.

For analysis purposes, an ice spike was defined to be a distinct projection from the ice surface of length 0.5 cm or greater. The total number of cubes with ice spikes was counted, and this number was divided by 50 to estimate the probability of ice-spike formation for the given conditions. Further trials were sometimes necessary and are reflected in reduced error margins on the data plots.

3   Results

3.1   Observations

The experimental data are summarized in Figure 4. Pure water exhibited a probability of ice-spike formation of roughly 0.34. The separate addition of both calcium chloride and sodium bicarbonate in concentrations less than 10^{-5} molar resulted in a slightly higher probability of ice-spike formation, although this may have been purely due to experimental error. With increasing concentrations, the two salts showed similar behavior, drastically reducing the probability of ice-spike formation. These results are consistent with the results of a previous study using sodium chloride [14]. Both methanol and ethanol, added separately to water, significantly facilitated the formation of ice spikes, only producing an inhibitory effect at concentrations greater than or equal to 10^{-3} molar. Acetic acid produced a larger inhibitory effect than other solutes at very low concentrations, but behaved in a similar manner as as the two salts at concentrations greater than 10^{-5} molar.

In addition to the number of ice spikes, the appearance of the frozen cubes was also observed. Two effects were found to occur at high concentrations. The first was a smoothing of the surface of the cube. Cubes consisting of pure, or nearly pure, water usually exhibit a few millimeter-scale lumps distributed randomly over the surface—features which were almost entirely absent in cubes of solutions of impurity concentration greater than 10^{-3} molar. Although no quantitative data were recorded, the appearances of ice lumps and ice spikes seem highly correlated. The second effect was a change in the appearance of the insides of the ice cubes. High concentrations of acetic acid, methanol, and ethanol sometimes produced cubes that were nearly transparent. Pure water cubes exhibited a cloudy appearance due to gases in the water which came out of solution during freezing, leaving bubbles.
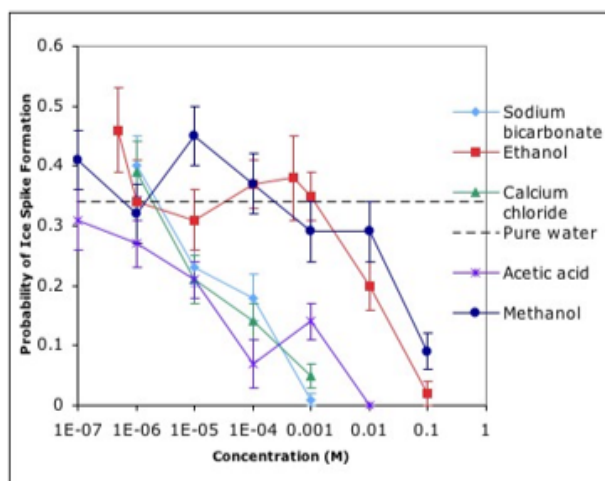
Figure 4: Consolidated experimental data. Concentrations are molar. Data for sodium bicarbonate (NaHCO$_3$), calcium chloride (CaCl$_2$), and acetic acid (CH$_3$COOH) were similar, producing a large inhibitory effect at relatively low concentrations. Ethanol (CH$_3$CH$_2$OH) and methanol (CH$_3$OH) exhibited no inhibitory properties at low concentrations and required roughly 100 times the concentration of the other solutes to have a similar inhibitory effect.

3.2 Sources of Error

This experiment was designed to determine general trends, so minimizing error was secondary to acquiring substantial amounts of data. Error bars shown in plots are one standard deviation, calculated using Bernoulli statistics. In addition to random error due to vibrations and minute temperature fluctuations, there were several sources of systematic error in this experiment, most of which were considered inconsequential. The first of these was the inaccuracy of the concentrations of the solutions frozen. Volumes were measured in a 300 mL beaker accurate to about 3 mL and in a 2 L beaker accurate to about 10 mL. Masses were measured with an electronic balance accurate to 0.1 g. These instruments may have contributed an error of as much as 10% in the concentrations, which was judged harmless due to the logarithmic distribution of trial concentrations.

There were two main sources of human error. The first was in the identification of ice spikes. The criteria were subjective, and verification of appropriate length was accomplished by eye, without use of a ruler. The second was in the placement of the ice-

cube trays on the wire rack, which varied slightly from trial to trial. Both of these sources of error could have been addressed, but this would have required a prohibitive amount of time and reduced the amount of data collected.

4   Discussion

The data prompt many questions about the ice-spike phenomenon. The presence of impurities can clearly inhibit ice-spike formation, and this effect becomes more prominent at higher concentrations. However, a preliminary model for ice-spike inhibition based on freezing-point depression seems unlikely due to the scale of the concentrations involved. For instance, a 0.001 molar solution of CaCl$_2$ would depress the freezing point of water by only 0.006°C, which is far smaller than the scale of random temperature fluctuations within the freezer. Nevertheless, ice spikes were seven times less likely to occur in 0.001 molar calcium chloride than in pure water. The highest freezing-point depressions in the experiment, those for the 0.1 molar alcohol solutions, were only 0.186°C, a negligible amount. Moreover, the probability of ice-spike formation at a given concentration varied widely between solutes, suggesting that colligative properties are not at work. The data suggest that freezing-point depression could only play a significant role given two rather unlikely conditions. The first is that solutes reach concentrations orders of magnitude larger in drops at the tips of ice spikes than in the original solution. The second is that the scale of this amplification effect varies widely between solutes. A future experiment comparing concentrations of solutes at the tips of ice spikes with concentrations in the rest of the cube could investigate this model.

Since freezing-point depression is an unlikely source of ice-spike inhibition, a more likely model is based on crystal formation. According to the Bally-Dorsey model, ice spikes form when most of the surface of the water is frozen, leaving only a small hole. The convergence of three dendritic crystal sheets usually forms this triangular hole, which becomes the base of the ice spike. Inhibition of the formation of these sheets could easily account for reduced probabilities of ice-spike formation at large concentrations. Though this model seems promising, the dependence of crystal formation on the chemical properties of the substance is not well understood. An experiment directly observing crystal growth in water as a function of the concentration of chemical additives would be

necessary to investigate this model.

Qualitative observations of ice lumps and transparent cubes present numerous avenues for future research. It is possible that the ice lumps observed at low concentrations are formed in a manner similar to ice spikes, whereby liquid water is pushed out through a hole in the nearly frozen surface. Lumps may be formed when water is pushed out too quickly, causing it to flow over the surface, or when the initial hole is too large, in which case the drop will freeze too slowly to lengthen into a spike. Since the appearance of ice spikes appears to be highly correlated with the appearance of ice lumps, it is likely that the same factors lead to the inhibition of both. The transparency of some cubes at high concentrations is a more perplexing phenomenon, as there is no readily apparent mechanism for the dissipation of dissolved gases. This effect was only observed in the presence of liquid solvents, perhaps indicating that dissolved solids and liquids may accumulate differently in the ice during freezing. The correlation between the transparency of ice cubes and the inhibition of ice spikes could not even be qualitatively established within the context of this experiment. A longer study might make more careful inspections of the cubes in addition to testing more solutes to gain a better understanding of this effect.

5 Conclusion

Chemical additives in water have been found to inhibit the formation of ice spikes. Metallic salts have been found to inhibit the formation of ice spikes to a large extent, even at low concentrations. Alcohols have been found to promote the formation of ice spikes, inhibiting ice-spike formation only at concentrations greater than or equal to 10^{-3} molar. This experiment has not supported a model of the inhibition of ice spikes based on freezing-point depression, but has suggested one based on the formation of dendritic sheets.

6 Acknowledgments

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