

BOILING POINT OF AQUEOUS METHANOL SOLUTIONS

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ABSTRACT

We hypothesized that the boiling point of methanol would increase linearly from the traditional boiling point elevation equation. We boiled various percentages of methanol-water solutions, graphing the temperature versus time to see at what temperature the methanol in each solution boiled. Our graph of all boiling points versus the square root of molality of our methanol-water solutions was inversely exponential, meaning our hypothesis was incorrect. Because the boiling point elevation equation was ineffective for predicting the boiling point of methanol-water solutions, we developed an equation from our data that can be used to determine the boiling point of methanol when mixed with water in different percentages.

INTRODUCTION

The purpose of this experiment was to evaluate how the boiling point of methanol would be affected when it was mixed with water. This research began as preliminary research for another experiment, but soon became the focus of our work. We were originally interested in the effect of other things such as sodium chloride (NaCl) and sand/gravel on methanol's boiling point, but soon discovered that water and methanol in various proportions behaved oddly.

Methanol is an alcohol with the molecular formula CH_3OH . Traditionally, alcohols are miscible (soluble in all proportions) with water. A solution is miscible when two things completely mix. This happens when the intermolecular forces between substance A and substance B are stronger than the intermolecular forces between substance A and itself, which is the case with methanol and water. Solutions that interact also tend to alter boiling points of the solute and solvent(s). Boiling point is determined by how much energy in the form of heat is required to break the bonds of the substance. When two things are mixed together, their different charges, electronegativities, partial dipoles, or dispersion forces interact with each other, and this creates new types of bonds, and consequently new boiling points for the solvent and solute(s).

For example, water's boiling point is 100°C . The electro-negativity difference between hydrogen and oxygen is large, and so we end up with a large concentration of electrons around the oxygen atom of the molecule. This creates strong dipoles among water molecules, allowing for hydrogen bonds to form between the positive dipoles of hydrogen atoms and the negative dipoles of oxygen atoms in adjacent water molecules. When an ionic solid like NaCl is added, ion-dipole forces between the charged ions and oppositely charged water dipoles form hydration shells of water molecules surrounding an ion from the solute. These hydration shells (which are also attracted to each other) restrict movement and form an interconnected system which is harder to break apart than either of the pure substances. Systems also tend towards levels of higher entropy, and a solution provides more opportunities for different interactions than either the pure solvent or solute. Subsequently, the boiling point of water increases according to the amount of solute that is dissolved in it due to ion dipole forces and the increased entropy of the system.

The equation for the changing of a solvent's boiling point when a solid ionic solute is dissolved in it is given by $\Delta T_B = K_B m$, where K_B is a solvent-specific constant with units $^\circ\text{C}/m$ and m is the molality of the solution. No textbooks, including Silberberg's *Chemistry* and other college-level chemistry resources, or websites indicated that this equation would not also apply to two miscible liquids. However, none of the sources said it would either. Our hypothesis was that the boiling point elevation would apply to our miscible solution of methanol and water, largely because we never found any source that refuted that assumption. We were however, skeptical from the beginning because all of the example problems dealt with solvent-solution situations such as NaCl and water, and never with two liquids, much less ones that did not dissolve each other. If we discovered that the ionic solvent equation did not work for methanol and water, our aim was to find an equation that did.

HAZARDS

Methanol is slightly toxic by skin absorption and inhalation. As an alcohol, it evaporates rather quickly. It is not necessary to specifically avoid inhaling methanol, but prolonged exposure to large amounts of vapor could be harmful. Should a spill of a large amount occur, be careful not to breathe it in constantly. To avoid breathing in more than is absolutely necessary, do not leave methanol containers open for prolonged periods of time and do not leave them in an area of direct sunlight or other heat source.

Methanol is also flammable, and because this experiment involves quite a bit of heating and boiling, it is a good idea to always keep stock methanol, spare methanol and other samples a good distance from the hot plates or other hot items.

Use Plexiglas Florence flasks to help manage wear and tear. Constant heating and cooling of glassware causes small cracks to form, and in some cases causes glassware to break. Should you notice a break, do not use the broken item. Should a break or hairline break occur during heating or cooling, remove the heat source and allow the solution to settle and cool to room temperature before disposing of the glassware and sample.

MATERIALS

The number of various materials you will need depends on how many trials you want to do at once. The maximum number of trials we performed simultaneously was four, and additional trials as necessary.

Materials:

Ringstands
90° clamps
Rod clamps
Hot plates
Vernier LabPro
Vernier LoggerPro 3.4.1

Eye dropper

Vernier Graphical
Analysis 3.1.1
Vernier stainless steel
temperature probes
250 mL Florence flasks
Electronic balance

Appropriate stoppers
(Size 5)
Methanol (CH₃OH) -
anhydrous (absolute)
De-ionized water

METHODS

1. A cleaned Florence flask was used and filled with 50.0g of methanol and 50.0g of water to make a 50% methanol by mass solution. Then, a stopper was placed on the flask.
2. The flask placed on a hot plate and clamped in place with the ringstand and clamps.
3. A temperature probe, attached to a LabPro and computer, was clamped onto the ringstand above the flask such that it could be lowered in. A diagram of the setup is provided below in Figure 1.
4. The stopper was removed and the hot plate was set to "9" (this would be whatever setting allows the temperature of the hot plate to reach 100° C). The temperature probe was then lowered into the liquid and allowed to heat as data was collected on the computer. Temperature readings were collected at a rate of 120 samples per minute.
5. Steps 1-5 were repeated with 90, 80, 70, 60, 40, 30, 25, 20, 15, 10, and 5% methanol (by mass) solutions.

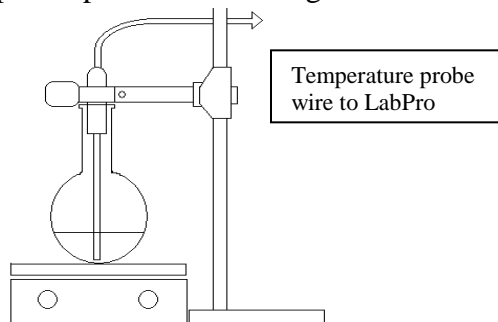


Figure 1

DATA/CALCULATIONS

Once the methanol was boiled off (the graph of temperature was no longer flat-lining), the graph of the data was analyzed. Where a clear area of flat-lining took place (indicating a change from liquid to gas), the first 120 samples were averaged to determine the boiling point of the methanol in that solution. Figure 2 shows the percentage of methanol in all of our solutions, the experimental boiling point (by average of 120 samples), and the elevation from pure methanol's boiling point. The only anomaly in our data collection was the experimental boiling point of 40 percent methanol. At this percentage we recorded an 81.79 °C boiling point, which was less than that of 50 percent methanol (82.92 °C). This did not follow the general trend of increasing boiling point with decreasing percentage methanol.

% Methanol	B.P. (°C)	B.P. Elevation (°C)
90	69.04	4.34
80	73.84	9.14
70	77.73	13.0
60	79.49	14.8
50	82.92	18.2
40	81.79	17.1
30	85.57	20.9
25	87.95	23.3
20	89.49	24.8
15	91.14	26.4
10	92.64	27.9
5	96.03	31.3

Figure 2.

As we boiled off various solutions of different methanol-water percentages, we observed that the methanol boiled at higher temperatures as the percentage of methanol was lowered. The boiling point of water was not affected because the water increased the methanol's boiling point. Any excess water did not have anything to interact with. As the

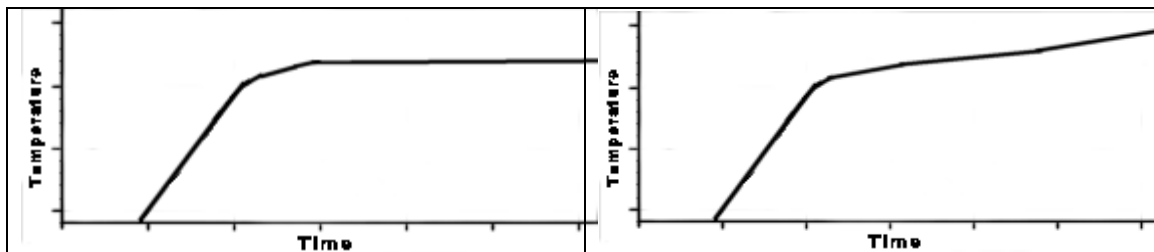


Figure 3.: 80% Methanol

Figure 4.: 30% Methanol

percentage of methanol was lowered, particularly below 20 percent by mass, the flat-lining of temperature on a graph of temperature measurement that normally occurs during boiling became shorter and more difficult to define. The area of the temperature graph that was predominantly flat also became increasingly slanted, as is seen in the comparison between the temperature graph of 80 percent and 30 percent methanol (Figures 3 and 4 shown above). These trends are also apparent over the whole span of percentages (see Appendix A, Figures 2-13).

$$\Delta T = K_b m = (.83 \text{ }^\circ\text{C}\cdot\text{mol/kg})(55.51 \text{ kg/mol}) = 46.07 \text{ }^\circ\text{C}$$

Figure 5.

The boiling points we recorded for each solution of methanol (by averaging 120 temperature samples at what appeared to be the first flat-lining of the temperature graph) were increasingly erratic. They were also significantly different than the values we predicted using the boiling point elevation equation (BPPE) for solutions (see Figure 5) which we hypothesized would predict the boiling point of the methanol. A table of several predicted and subsequent experimental boiling point differences for methanol mixtures can be found in Figure 6 (assuming a boiling point for pure methanol of 64.7 °C and a K_b of .83 for pure methanol. As is apparent, even a mixture of 50 percent methanol would force methanol's boiling point above the boiling point of water by the BPPE (Figure 5).

% Methanol	Predicted Δ B.P. (°C)	Experimental Δ B.P. (°C)
90	5.12	4.34
70	19.75	13.03
50	46.07	18.22
30	107.5	20.87
10	414.7	27.94

Figure 6.

Our experiments showed that the boiling point of our solutions increased in a non-linear fashion as the percentage of methanol decreased. While the values predicted by the BPPE continued to rise to outlandish values, our experiments showed that the rate at

which the boiling point of methanol was rising seemed to level off as the percentage of methanol approached zero.

DISCUSSION

Contrary to our hypothesis that the BPEE would apply to our methanol-water solutions, our experiments showed that temperature predictions made using the BPEE were significantly larger than the experimental boiling points (see DATA/CALCULATIONS, Figure 6). The non-linear relationship between the molality and the boiling point of our solutions alerted us that a linear approach to plotting (and equation-development) of our data would leave some experimental data points incompatible with the plotted equation. We realized we would have to develop a new equation for the prediction of methanol's boiling point due to the immense difference between our experimental data and the predictions made by using the BPEE (see DATA/CALCULATIONS and Figures 5 and 6). We decided to calculate the square root of the molality of each methanol solution for plotting purposes against the experimental boiling points. We used the equation given in Figure 8, where methanol is the solvent (because its boiling point was always the one affected) and m is the molality of the solution.

$$\sqrt{m} = \sqrt{\frac{\left(\frac{g_{H_2O}}{\text{molarmass}_{H_2O}}\right)}{kg_{CH_3OH}}} = \sqrt{\frac{\left(\frac{25g_{H_2O}}{18.0148g_{H_2O}}\right)}{.025g_{CH_3OH}}} = 7.451 m^{1/2}$$

Figure 8.

Using Vernier Graphical Analysis 3.1.1, we plotted the \sqrt{m} of each methanol solution against the subsequent boiling point. We then tried to fit a graph to our data which would satisfactorily lie on or as near as possible to all of our plotted points. The graph produced is shown in Figure 9. (To see the graph laid overtop our points of data and an accompanying table of the percentage methanol, \sqrt{m} , and boiling point ($^{\circ}\text{C}$) of all solutions, see Appendix A, Figure 1) The equation defining this graph is shown in Figure 10. In essence, this equation can be used to predict the boiling point of the methanol in a solution of methanol and water of a given molality, or to calculate the molality of a methanol-water solution given the boiling point of the methanol (provided a boiling point can be identified with relative confidence).

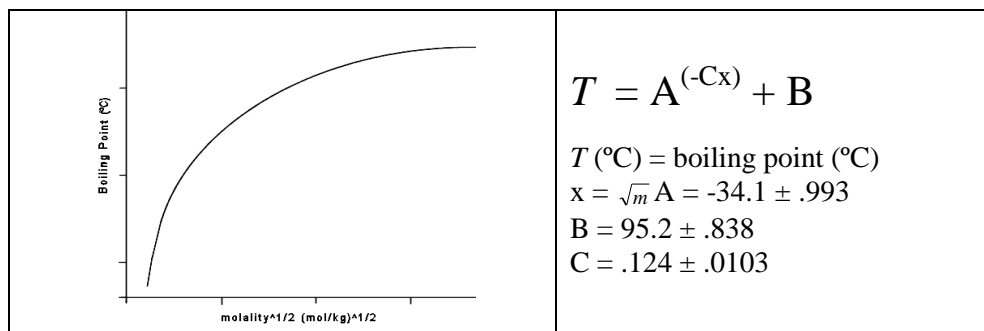


Figure 9.

Figure 10.

We then wanted to adjust our equation to take into account that our experiments were not being performed at sea level (1.0 atm). We recorded the pressure in our lab over three days, taking multiple readings each day during varying weather. We averaged these values, finding a general pressure of 100.85 kPa for our lab. Rearranging the equation as shown in Figure 11, we found that the comparable temperature (°C) at sea level (at a pressure of 1.0 atm, or 101.3 kPa) equaled our recorded temperatures multiplied by a constant of 1.004. This made any temperature adjustment to our recorded boiling points effectively insignificant, leaving our equation (Figure 10) unchanged.

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad T_{SL} = \frac{P_{SL}T_E}{P_E} \quad T_{SL} = \frac{(101.3KPa)(T_E)}{100.85KPa} \quad T_{SL} = 1.004(T_E)$$

where X_{SL} = variable at sea level and X_E = variable at our experiment location

Figure 11.

Error in our experimental boiling points (see the deviations from the general pattern in Appendix A, Figure 7) is due, at least in part, to the difficulty of identifying where our graphs of temperature genuinely flat-lined. As can be seen in our temperature graphs (Appendix A, Figures 2-13), the period of time where methanol was actually boiling became increasingly ambiguous as the percentage of methanol in the solution dropped. This probably occurred because a small amount of methanol does not require a long period of time to boil off. This caused the flat-lining of the graph to become more heavily intertwined with the rising in temperature of the larger percentage of water.

The complexity of our developed equation can be attributed to its (perhaps overly) exact manner in matching data, but mostly to the erratic nature in which the boiling point of methanol is altered by the analogous behavior methanol and water show when mixed (see INTRODUCTION). The large constants are due mostly in that we chose to graph \sqrt{m} against the final boiling point, rather than the boiling point elevation. It would also be beneficial to see if any sort of constant can be identified for solvents other than methanol that would allow for our equation to be used, much as the BPEE is used.

We theorize that the analogous behavior of aqueous methanol is due to methanol's slightly polar nature. With the molecular formula CH₃OH, methanol can be considered slightly polar because of the highly negative O atom, which gives the C of the molecule a slightly positive charge by proximity. This polarity may allow for hydrogen bonding within an aqueous methanol solution, easily raising the amount of energy needed to break the bonds of the methanol and water, subsequently raising the boiling point. Methanol creates a 'shell' around the water molecule, and this methanol may interact with another 'shell' around it, much like hydration shells seen in ionic solutions.

The unusually high boiling point of methanol when compared with other alcohols may be caused by methanol's small size, allowing the methanol molecules to get close enough to each other to form the bonds needed for a 'blanket' of methanol around the water molecule. Longer-chain alcohols would have their -OH end attracted to the water molecule, but the remaining chain would have no charge, and could subsequently attract no more (or very few) additional alcohols, disallowing for a buildup of an alcohol fabric

as seen with methanol. The boiling of water is not affected because by that point the methanol has already been boiled off, disallowing for any stronger bonds than the cohesion water already has.

We theorize the elevation of methanol's boiling point increases with the decrease of mass percentage methanol due to the difference in the strength between methanol-water bonds and methanol-methanol bonds. With more methanol, the shell that surrounds the water molecule is made more completely of methanol, which is full of bonds which can be broken at lower temperatures. With less methanol, however, a shell of methanol may surround the initial water molecule, which is then surrounded by water in subsequent layers. This methanol-water bond is stronger, causing a higher boiling point.

APPENDIX A

Figure 1: Overall Equation and Table

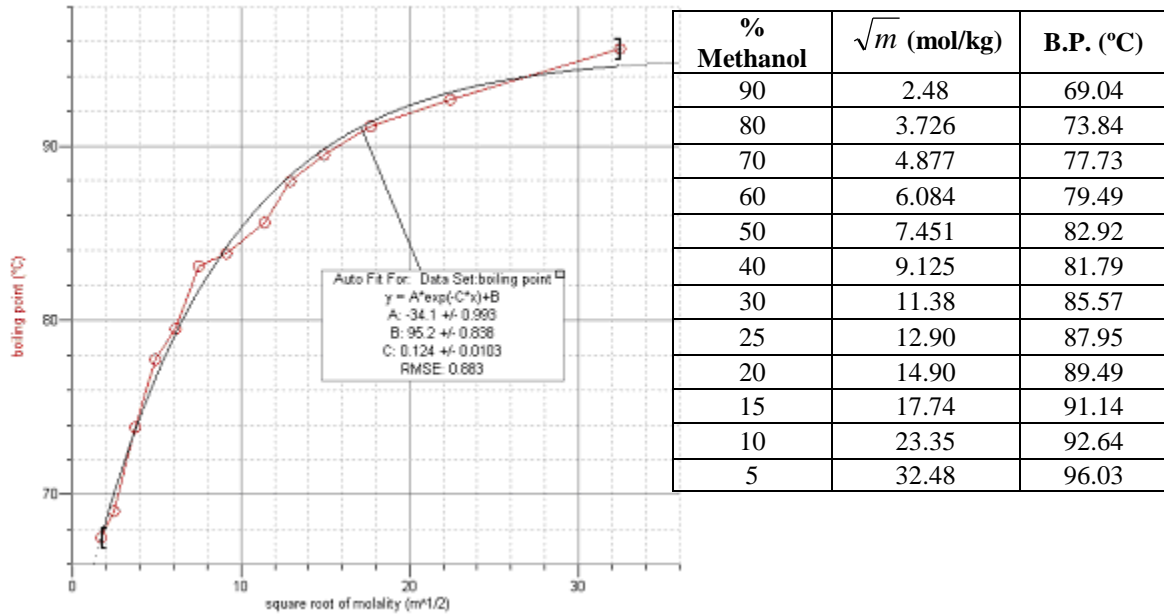


Figure 2: 90% Methanol

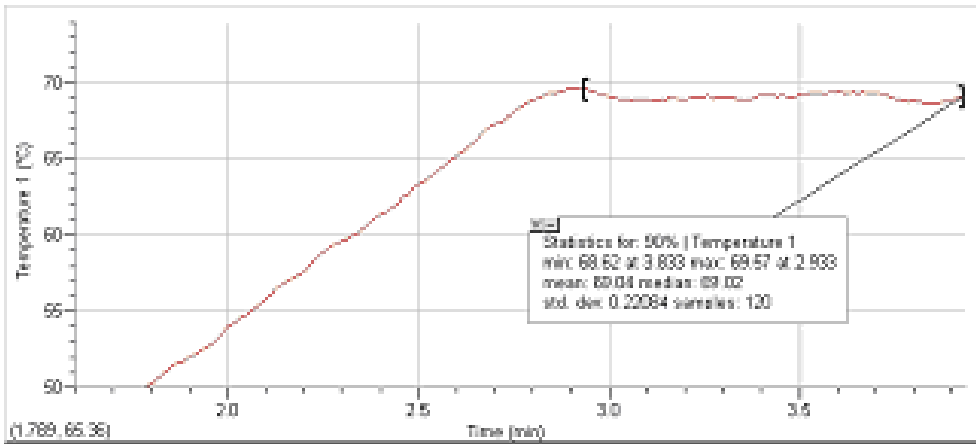


Figure 3: 80% Methanol

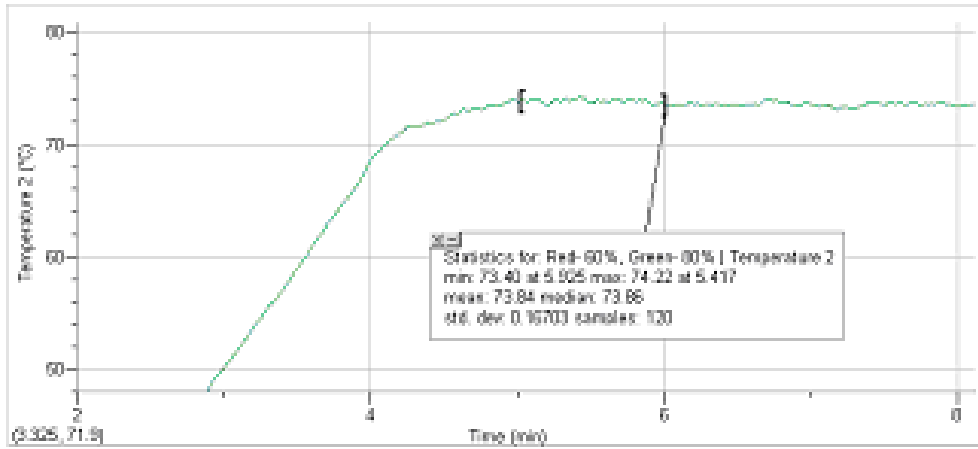


Figure 4: 70% Methanol

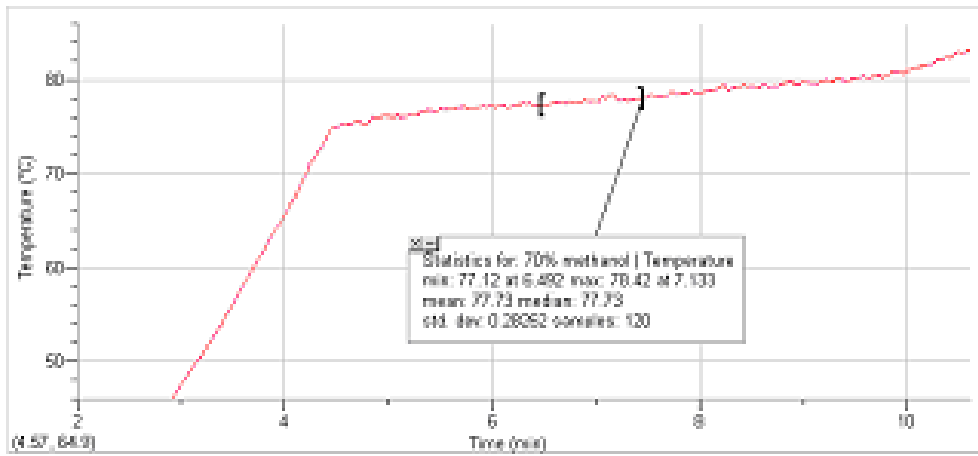


Figure 5: 60% Methanol

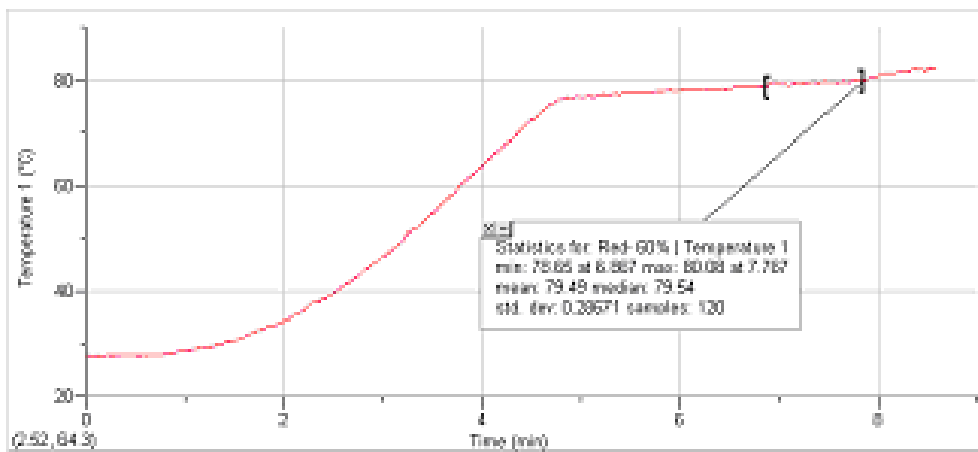


Figure 6: 50% Methanol

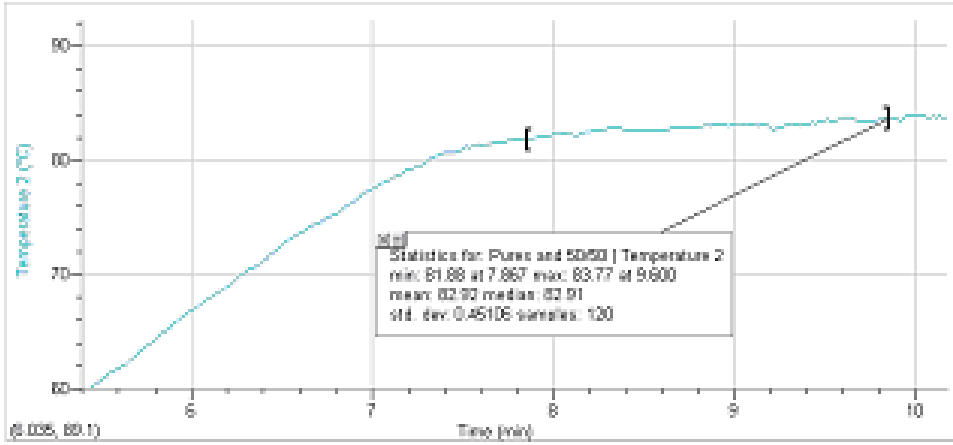


Figure 7: 40% Methanol

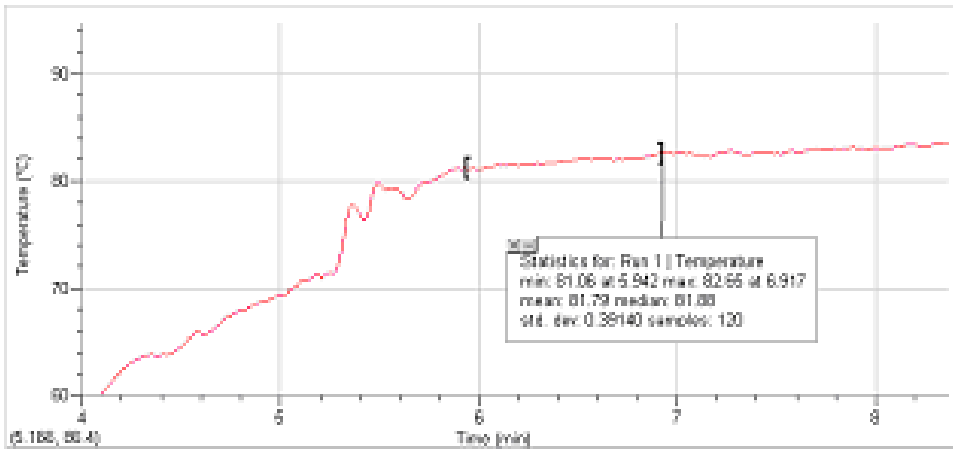


Figure 8: 30% Methanol

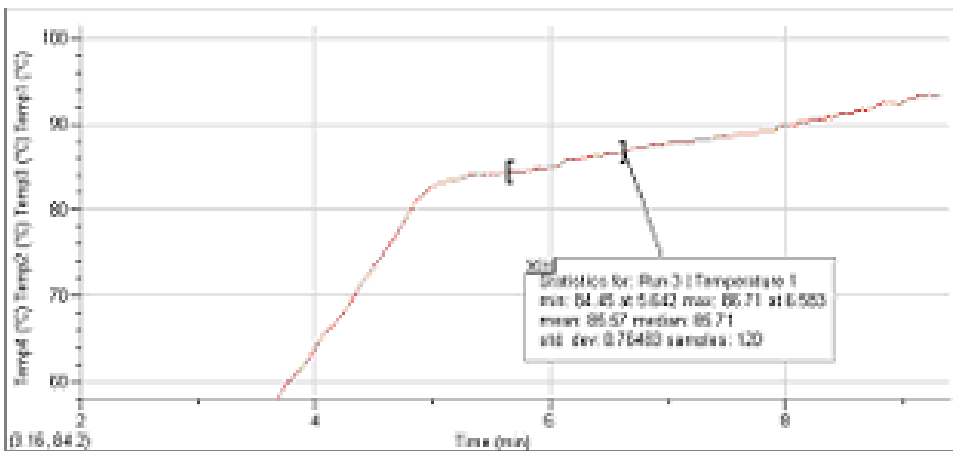


Figure 9: 25% Methanol

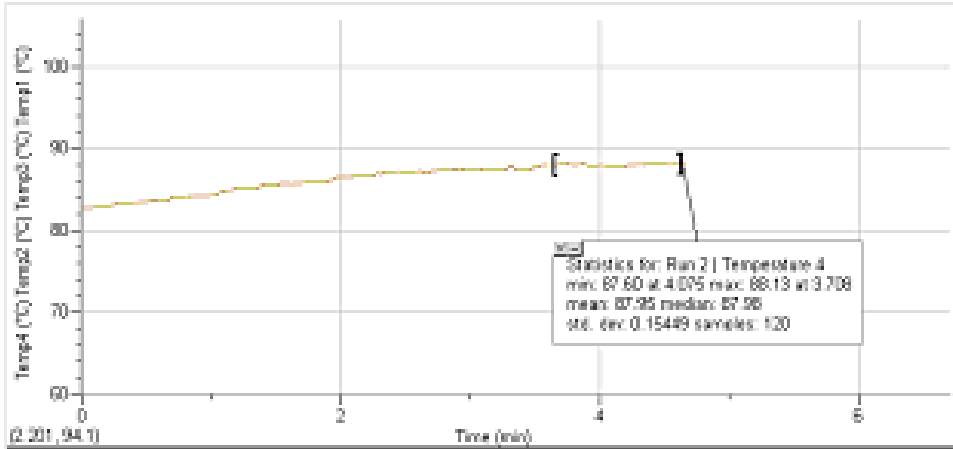


Figure 10: 20% Methanol

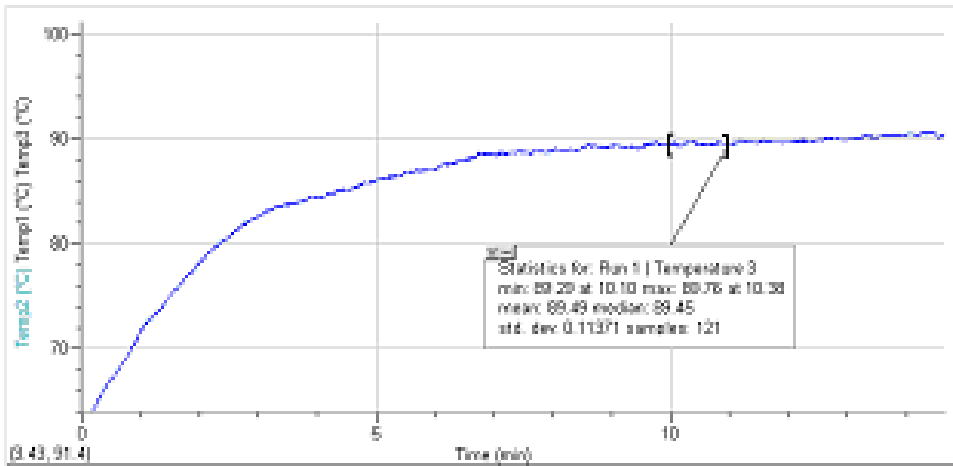


Figure 11: 15% Methanol

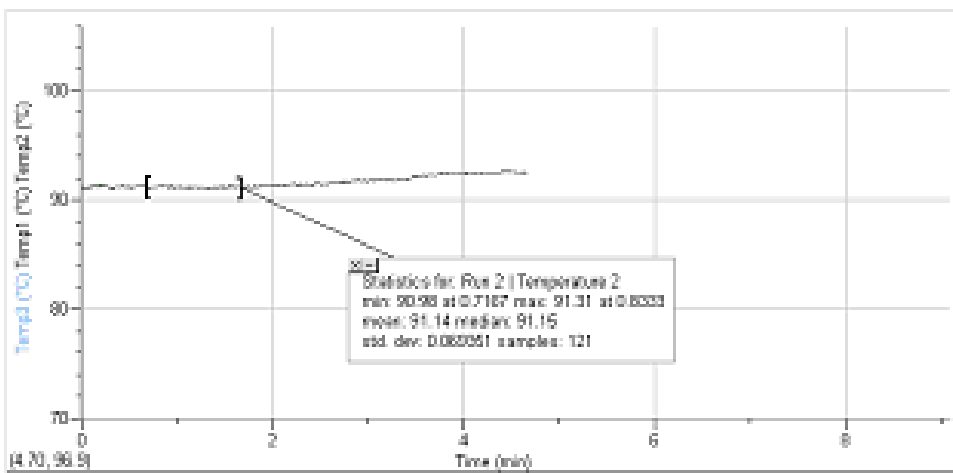


Figure 12: 10% Methanol

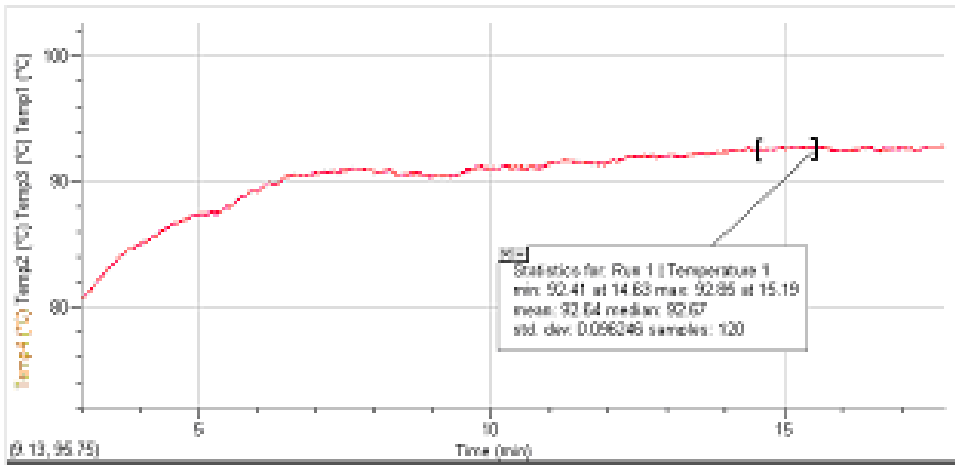
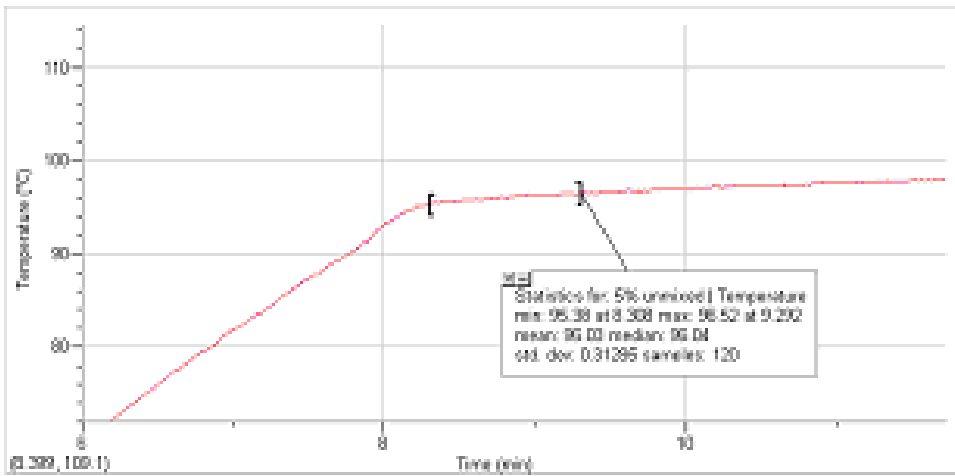


Figure 13: 5% Methanol



Works Cited

- "Chapter 15: Colligative Properties of Solutions." LSU Department of Chemistry.
Louisiana State University Department of Chemistry. 05 May 2006 <[http://72.14.207.104/search?q=cache:qCpNAUw73GYJ:chemistry.lsu.edu/webpub/1202-Notes/Solutions-Colligative-Props.doc+Chapter+15+Colligative+properties+of+solutions &hl=en&gl=us&ct=clnk&cd=3](http://72.14.207.104/search?q=cache:qCpNAUw73GYJ:chemistry.lsu.edu/webpub/1202-Notes/Solutions-Colligative-Props.doc+Chapter+15+Colligative+properties+of+solutions&hl=en&gl=us&ct=clnk&cd=3)>.
- Dougan, L., et al. "Methanol-water solutions: A bi-percolating liquid mixture." The Journal of Chemical Physics Volume 121. Issue 1301 Oct 2004 6456-6462. 20 Apr 2006 <<http://scitation.aip.org/getabs/servlet/GetabsServlet?prog=normal&id=JCPSA6000121000013006456000001&idtype=cvips&gifs=yes>>.
- Guo, J.-H.. "Why Alcohol and Water Don't Mix." The Advanced Light Source. 10 Dec 2003. The Advanced Light Source. 01 May 2006 <http://www-als.lbl.gov/als/science/sci_archive/70methanolmix.html>.
- Silberberg, Martin S.. Chemistry: The Molecular Nature of Matter and Change. Fourth. New York, NY: McGraw-Hill, 2006.
- "The Land that is Pennsylvania." Pennsylvania Historical and Museum Commission.
Pennsylvania Historical and Museum Commission. 01 May 2006
<<http://www.phmc.state.pa.us/bah/pahist/natural.asp?secid=31>>.