Investigating the Relationship between Variance of Transition Temperatures in an Undergraduate Laboratory Setting

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SUMMARY

Colligative properties are properties of impurities. Most substances are mixtures since it is difficult to maintain a completely pure substance. The effects of a solute on the properties of a substance include freezing point depression (FPD) and boiling point elevation (BPE). These properties are due to the impurity lowering the mole fraction of the solvent, consequently decreasing its chemical potential. This stabilizes the liquid state and causes the solvent to exist as a liquid for a wider range of temperatures at constant pressures. The purpose of this study is to investigate a general relationship between FPD and BPE. Specifically, this study aims to provide a method in determining a proportionality between the transition constants of a general solvent. The transition constants represent how much the variance of transition temperatures change against varying concentrations of solute. The transition constants (K_{fp} and K_{bp}) are determined for water with varying concentrations of dissolved acetic acid, sucrose, and sodium chloride. The freezing point and boiling point of the solutions is determined with analysis of cooling and heating curves, and the variance of transition temperature is determined upon comparison with pure controls. BPE has been found to be positively correlated with FPD, increasing by a factor of 0.35 (± 0.09 s.d.). The experiments designed in this study provide a simple reproducible way of demonstrating and supporting the fundamental principles underlying colligative properties.

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INTRODUCTION

Colligative properties are exhibited as a change in physical properties of a solvent with a dissolved solute. Examples of colligative properties are freezing point depression (FPD), boiling point elevation (BPE), osmotic pressure depression (OPD), and vapour pressure depression (VPD). These properties depend simply on the ratio of the number of solute particles to the number of solvent molecules in a solution. In other words, the chemical reactions of the different substances within the solution are not important factors when investigating the colligative properties of solvents. As such, the significant value of measure that determines the effects of a solute on a solvent is the van't Hoff factor of substances. This value allows for colligative properties to be measured upon apparent concentrations of solute particles within solution rather than the molecular concentration. For example, dissolving 1 mole of sodium chloride (NaCl) in water yields an apparent concentration of 2 moles within solution since each molecule of this substance dissociates completely in water to produce 2 ions, Na^+ and Cl^-. Furthermore, a substance that does not dissociate into parts upon solvation has a van't Hoff factor of 1. These values do not necessarily have to be integers depending on the nature of the solute. For example, acetic acid (CH_3COOH) solvated by water has a van't

Hoff factor of neither 1 nor 2. Acetic acid is a weak acid that may dissociate into its conjugate base and a hydronium ion, which would suggest that it should have a van't Hoff factor of 2. However, since it is a weak acid, it does not dissociate completely, i.e. some molecules in the solution are not dissociated and would thus have a van't Hoff factor character of 1. Therefore, acetic acid actually has a van't Hoff factor of 1.05. It is important to define and consider van't Hoff factors of solutes when observing colligative properties in order to properly draw conclusions upon investigation.

The liquid state is the mediating state of matter between the most rigid structures and the most free-flowing fluids. It is an important state of matter because of its properties of maintaining a dynamic system while remaining contained within a space. Chemists use the liquid phase because reactions can happen much more quickly and in a more controlled fashion within solution. This study looks at the stabilization of the liquid state as a result of solutes dissolved in the mixture. The depression of freezing point temperature and the elevation of boiling point temperature are the observed physical changes caused by the presence of solvated particles. The application of FPD is prevalent especially during winter as salt is dissolved in the water to prevent it from freezing. Changing the concentration of dissolved solutes is positively correlated to changing the amount by which the transition temperature of the solvent depresses or elevates. In other words, a certain amount of solute dissolved in a solution causes the freezing point to decrease a certain amount and if a greater amount of that same substance is dissolved, then the freezing point would decrease a greater amount. This also applies to the elevation of boiling point. Finding a relationship between these two properties would allow for the techniques developed in this experiment to be used to demonstrate and support the fundamental principles underlying colligative properties.

This study aims to answer the question of whether or not the freezing point depresses at the same rate at which the boiling point elevates about the same changes in dissolved solute concentration. In order to answer this question, a reproducible method for determining each the freezing point and boiling point must be used. This study uses the analysis of cooling and heating curves that map out the temperature of the solution over time. Temperature is simply a measure of the average kinetic energy of the particles in the solution. Observing an increase in temperature upon heating a substance is due to the energy transfer converting the thermal energy from the heat source into kinetic energy in the substance. However, thermal energy introduced to a system can also allow for intermolecular bonds, such as hydrogen bonds between water molecules, to break. The state of matter of a system is determined by the amount of intermolecular bonds exhibited between molecules of the substance. Less intermolecular bonds are exhibited in a gas than in a liquid, and more intermolecular bonds are exhibited in a solid than in a liquid. In a transition of state, the thermal energy transfer is used for the breaking of intermolecular bonds in melting and vaporization, and for the making of bonds in condensation and freezing. Thus, there is no thermal energy transfer contributing to the kinetic energy of the system. This would be exhibited in a cooling or heating curve as a plateau in temperature as the substance is changing state. This plateau can be easily extrapolated to determine the temperature at which the state transition occurs and can thus determine the freezing and boiling points of various solutions. FPD and BPE are then determined by calculating the difference between the transition temperature of the solution and the transition temperature of the pure solvent control. The rate of FPD and BPE about changing concentration of solute particles is quantified as the transition constants: K_{fp} for freezing point and K_{bp} for boiling point. These constants can be determined through linear regression on the variance of transition temperature interaction with solute concentration.

If there is a relationship between FPD and BPE, then there would be a proportionality between the transition constants. If FPD and BPE change at the same rate, the regressions should be collinear and the ratio of transition constants (K_{bp}/K_{fp}) would be equal to 1. If FPD and BPE do not change at the same rate, but are proportional to each other, this would be observed by comparing the K_{bp}/K_{fp} ratio for multiple solutes and having the proportionalities be equal.

MATERIALS AND METHODS

This study investigated the change in the freezing point and boiling point of water in the presence of three solutes: sodium chloride (i=2), acetic acid

(i=1.05), and sucrose (i=1). The freezing point and boiling point of distilled water were determined and recorded as controls. Solutions of 0.45 mol/kg, 0.90 mol/kg, and 1.2 mol/kg of each solute were prepared in distilled water and tested with three replicate aliquots. 30 mL of each solution were prepared and three aliquots of 4 mL were taken in Pyrex® test tubes to be tested. The freezing point of each solution was also determined and the same frozen solution was tested afterwards to determine the boiling point.

Each solution was taken to freezing by submergence in an ice bath prepared by dissolving sodium chloride salt in a Styrofoam calorimeter cup containing a mixture of ice and water. Each solution was then taken to boiling by heating upon a hot plate in a heating block to evenly distribute the thermal energy among the solution.

Temperature of each solution through the transition processes was recorded with a PASCO® PASPORT Absolute Pressure/Temperature Sensor (PS-2146) and cooling/heating curves were constructed by a PASCO® SPARK Science Learning System (PS-2008A) interface.

Experimental data was exported and analyzed with Microsoft Excel 2013. A total of 30 cooling curves and 30 heating curves were constructed to determine freezing point and boiling point for each aliquot: 3 control aliquots, and 3 aliquots for 3 concentrations (0.45 mol/kg, 0.90 mol/kg, and 1.2 mol/kg). FPD is determined by subtracting the new freezing point from the freezing point of the distilled water control. Similarly, BPE is determined by subtracting the new boiling point by the boiling point of the distilled water control.

It is important to take the freezing point and boiling point of the solvent in which the query solutes are dissolved in because theoretical values are not necessarily reflected in practicality. As such, although theoretically water has a freezing point of 0°C and a boiling point of 100°C, the freezing point and boiling point determined by the protocol are different since there may be ions suspended in the distilled water. Since colligative properties are relative properties, it does not matter whether or not the solvent is pure.

RESULTS

It was determined that the freezing point of the distilled water control was -0.18 ± 0.01°C and the boiling point of the distilled water control was 101 ± 1°C. All freezing point and boiling point comparisons were taken from these values. The variance of transition temperature (ΔT_{tr}) values were plotted against concentration to compare the rate of BPE and the rate of FPD for sodium chloride, acetic acid, and sucrose dissolved in distilled water, as shown in Figure 1. Thus, it has been shown with this method that there is a proportionality between FPD and BPE and it is found that boiling point elevates at a rate slower than the depression of freezing point.

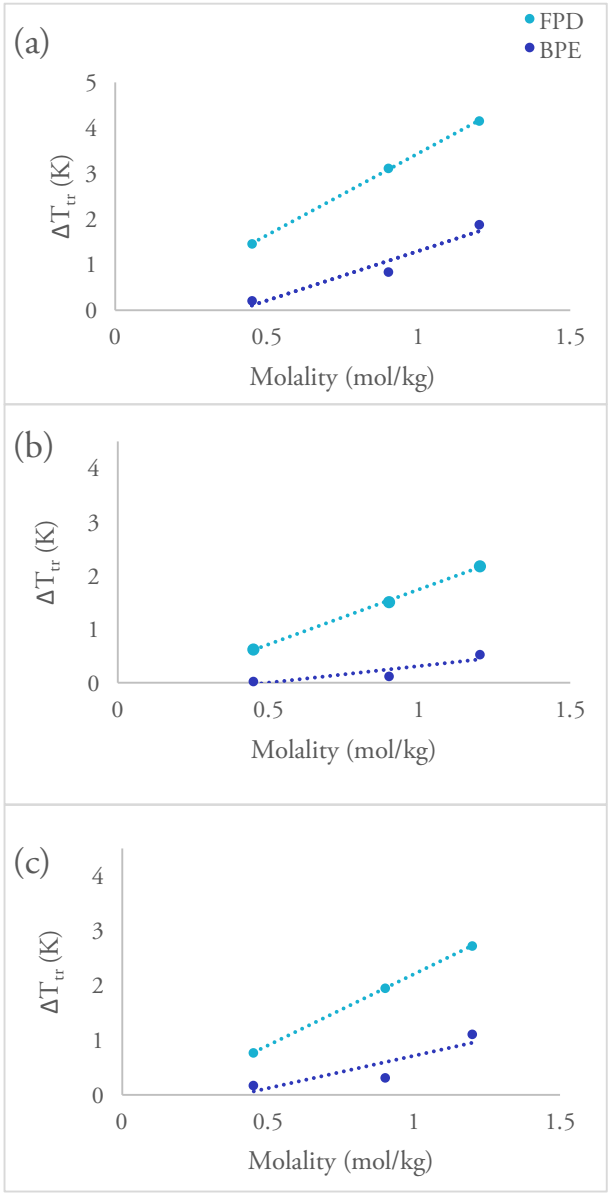

Figure 1: Variance of transition temperatures for (a) sodium chloride, (b) acetic acid, and (c) sucrose. FPD and BPE have been mapped on the same axes for comparison.

Table 1: Transition constants for sodium chloride, acetic acid, and sucrose.

	K_{fp} (°C/mol/kg)	K_{bp} (°C/mol/kg)	$(K_{bp}/K_{fp})/i$
Sodium chloride	3.6	2.2	0.3002
Acetic acid	2.1	0.63	0.3017
Sucrose	2.6	1.2	0.4536
			0.35 ± 0.09 s.d.

Qualitatively, there seemed to be no relationship between FPD and BPE as shown by the different slopes and by the absolute value of FPD being consistently higher than the absolute value of BPE. However, quantitatively, the rates at which these variance of transition temperatures change by concentration of solute are outlined in Table 1. Normalizing the proportionality by the van't Hoff factors of the solutes, it has been found that boiling point elevates 35% as quickly as freezing point depresses upon changing concentration.

DISCUSSION

The result of this study provides experimental evidence to support and demonstrate the relationship between FPD and BPE. An expression can be derived via the general relationship of colligative properties. In general, the rate by which the freezing point of a substance declines by the amount of dissolved solute is described as follows: $K_{fp} = \frac{M_A R T_m^{*\,2}}{\Delta_{\text{fus}} H_A}$ (Wang, 2009). Similarly, the rate by which the boiling point of a substance elevates by the amount of dissolved solute is described as follows: $K_{bp} = \frac{M_A R T_b^{*2}}{\Delta_{\text{vap}} H_A}$. Therefore, the proportionality of BPE against FPD can be determined simply by dividing the two expressions to arrive at the following expression:

$$\frac{K_{bp}}{K_{fp}} = \left(\frac{T_{bp,pure\ solvent}}{T_{fp,pure\ solvent}}\right)^2 \left(\frac{\Delta_{fus} H_{pure\ solvent}}{\Delta_{vap} H_{pure\ solvent}}\right).$$

This is a proportionality relating the variance of transition temperature in terms only of the pure solvent. In the case of water, as studied in this experiment, the boiling point and freezing point of water without any solute is 373.15 K and 273.15 K, respectively[2]. It is also known that the enthalpy of fusion of water at atmospheric pressure and at the freezing temperature is 333.5 J/g and the enthalpy of vaporization of water at atmospheric pressure and at the boiling temperature is 2260 J/g. With this information, the theoretical value that describes the rate at which the BPE of water increases in proportion to its FPD is 0.2754. In other words, theoretically, the BPE of water should increase 27.54% as quickly as the decline of FPD. Therefore, the results of this experiment were 73% accurate.

The experiments in this study could be incorporated in the thermodynamics laboratory curricula to provide an interactive way to teach colligative properties in addition to allowing students to develop skills in setting up experiments to answer specific research questions. This study only looked at water as the query solvent, however, a proportionality for different solvents such as diethyl ether could be calculated theoretically via the relationship expressed above and experimentally tested with the procedure provided in this study. Furthermore, this laboratory experiment has room for collaborative efforts in that groups of students could run this procedure for specific sets of conditions and all the data of every student could be collected and analyzed. The students can vary many parameters including: the solvent, the choice of solute, and the amount of solute dissolved. The students could also all run the same experiment and the same conditions and simply pool all the data to increase statistical significance and achieve more accurate results. The specific skills that the students will develop include: how to calculate molarity/molality, basic laboratory skills, statistical analysis, and Microsoft Excel. Overall, the experimental procedure designed in this study provide a simple and reproducible method of describing the theoretical phenomena of FPD and BPE to be applied as a pedagogical tool to teach students about the relationship between two colligative properties.

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REFERENCES

Ge X, Wang X., 2009. Estimation of Freezing Point Depression, Boiling Point Elevation, and Vaporization Enthalpies of Electrolyte Solutions. *Industrial & Engineering Chemistry Research*, 48 (4), 2229–2235.