EXPERIMENT 8

ANALYSIS OF BENZOIC ACID BY FREEZING POINT DEPRESSION

Objectives:

In this experiment, the molar mass of benzoic acid synthesized in Experiment 7 *Organic Synthesis-Hydrolysis of Methyl Benzoate* will be determined through the colligative property freezing point depression. Temperature measurements will be acquired using a Vernier temperature sensor and LoggerPro software to evaluate freezing points.

Background:

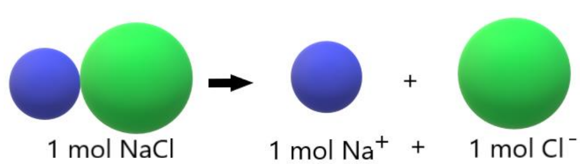
The depression of the freezing point of a **solvent** is directly proportional to the quantity of a **solute** dissolved in it according the following equation. The greater the concentration of solute the lower the freezing point.

$$\Delta T_f = iK_f(m)$$

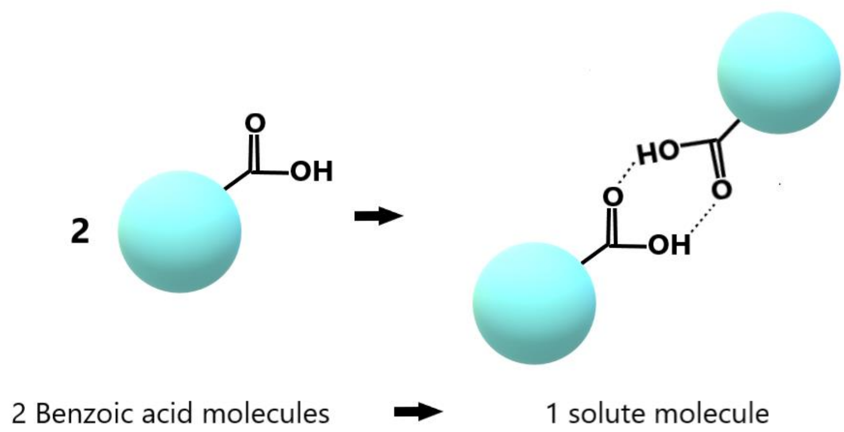
ΔT_f	Difference in freezing point between the pure solvent and the solution, $T_{f(\text{pure solvent})} - T_{f(\text{solution})}$
K_f	molal freezing point depression constant (constant for a given solvent)
m	molality of solution (moles solute/kg solvent)
i	van't Hoff factor

Because the freezing point of a solution is a **colligative property** (a function of the concentration of solute particles in solution) the freezing point can be used to evaluate purity of a substance and also can be used to determine the molar mass of a solute.

The van't Hoff factor in the above equation takes into account how solute molecules behave in a solvent. When the solute is stable and acts independently within the solvent, then i = 1. When a solute molecule **dissociates** (breaks up into its ions) in the solvent, such as NaCl in water, the **van't Hoff factor** will be greater than 1, depending on the extent at which the solute dissociates. For example, if all sodium chloride molecules dissolve into separate Na^+ and Cl^- ions then i = 2.



If the solute molecules interact with each other and **associate** (bind together) in the solvent, the van't Hoff factor will be less than 1 depending on the degree of association. Benzoic acid molecules can associate or bond with one another through hydrogen bonding of the carboxylic acid functional group. For example, if all benzoic acid molecules hydrogen bond with another then i = 0.5,

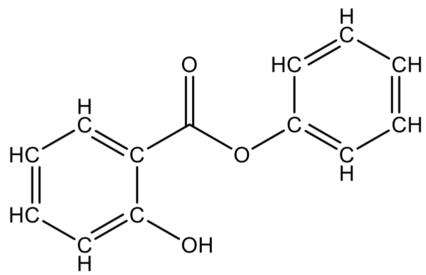
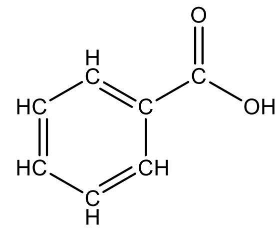


Hydrogen bonding of benzoic acid molecules has a direct effect on freezing point depression because it is a colligative property which is dependent on the number of solute particles in solution. The degree of association is dependent on the concentration of the solute in the solution therefore the van't Hoff factor must be experimentally determined. It should be noted that the freezing point depression constant, K_f, is a property of solvent and therefore is independent of the solute of the solution. The van't Hoff factor, i, is determined for a solution system (solvent + solute combination, at a specific solute concentration).

In order to determine the van't Hoff factor for the experiment, the freezing point of a solution of phenyl salicylate and commercially available benzoic acid will be determined. Using K_f for phenyl salicylate, i is calculated. The value for i indicates the degree of association of neighboring benzoic acid molecules. In the case where i= 0.5, all benzoic acid molecules are associated with another benzoic acid molecule resulting in half the amount of solute molecules in solution. Typically, 100% association is not seen and a van't Hoff factor between 0.5 and 1 will be found. Once the van't Hoff factor is determined, the freezing point of a solution of phenyl salicylate and your experimentally synthesized benzoic acid will be determined and the molar mass of benzoic acid calculated. Percent error calculation for the experimentally determined molar mass of benzoic acid and commercial benzoic acid will be a measure of purity of the lab synthesized benzoic acid.

The procedure thus involves the determination of three freezing points:

- Pure phenyl salicylate
- A solution of commercially available benzoic acid dissolved in phenyl salicylate
- A solution of experimentally synthesized benzoic acid in phenyl salicylate

Phenyl Salicylate (Solvent)	Benzoic Acid (Solute)
	
Molar mass = 214.22 g/mole K_f = 10.6 °C·kg/mol	Molar mass = 122.12 g/mole

All three freezing points will be found to be above room temperature. A hot water bath is used to bring the pure phenyl salicylate and three solutions to above the freezing point. The temperature of the liquid or solution is then monitored using a computer interface data acquisition system as it is cooled to room temperature and freezes.

Tasks to be completed:

1. Determine the freezing point of the pure solvent, phenyl salicylate.
2. Determine the freezing point of a solution of phenyl salicylate and commecial benzoic acid.
3. Determine the freezing point of a solution of phenyl salicylate and benzoic acid synthesized in the Experiment 7, *Organic Synthesis- The Hydrolysis of Methyl Benzoate*.
4. Calculate the molar mass of synthesized benzoic acid using experimental values and determine the purity of the product.

Experimental Procedure: To be completed in groups of 2 students.

Hardware and Software Initialization

1. Interface/Computer Initial Set-up
   a. Verify that the Logger Pro software is installed on the computer to be used and open it.
   b. Connect the Vernier interface to the computer.
   c. Connect the Temperature Probe to CH1 on the side of the interface.

2. Configure the Plot Display.
   a. Click on the graph to select it.
   b. Right click on the graph then select *Options* and *Column Options*. Alternatively, from the top menu select the *Options tab* then choose *Graph Options* and *Column Options*.
      - Choose *Temperature* and select the *Options* tab.
      - Change Displayed Precision setting to two decimal places.
      - Select Done.
   c. Right click on the graph. Select *Options/Graph Options*. Alternatively, from the top menu select the *Options tab* then choose *Graph Options*.
      - Select the *Axes Options* Tab.
      - Check the Temperature box for the y-axis and uncheck any other box that was checked by default. Select the autoscale feature for the y-axis. Do NOT select autoscale larger or autoscale to 0 feature.
      - In the drop-down box located in the x-axis section select Time and select the x-axis autoscale feature.
      - Select Done.

3. Configure the Data Collection.
   a. From the top menu bar select Experiment/Data Collection.
      - Select Timed Based Mode.
      - Set the length for 1 hour. Verify that the hour unit is selected.
      - Set the sample rate at 720 samples/hour. (This equates to a data being taken every 5 seconds)
      - Select Done.

I. Determination of the freezing point for commercial phenyl salicylate (solvent)

1. Fill the provided large beaker with hot water from the tap and place a large stir bar in the beaker. Heat the water on a hot plate **set on high** to near boiling with constant stirring. To maintain bath temperature, adjust the heat setting throughout the experiment. It may be necessary to add water as the volume decreases with heating.
2. Use a utility clamp to prepare a set-up to allow the monitoring of the temperature of the phenyl salicylate as it cools and freezes.
   a. Secure the larger, outer test tube in a utility clamp on a ring stand. This test tube is used to catch any solution in the event that the 6" test tube breaks.
   b. The entire set-up should be arranged so that the outer test tube is resting on the foot of the ring stand to prevent slipping while stirring.
3. Obtain a clean, dry 6" disposable test tube from the reagent table. Place the test tube in a 100 mL beaker and place both on a balance. Tare the balance. Remove the test tube from the balance and add approximately 5.00 g of phenyl salicylate to the test tube. Be very careful not to spill any of the phenyl salicylate. **It is not necessary to record this mass**.
4. Place the Vernier temperature probe and wire stirrer into the test tube containing the massed phenyl salicylate. Heat in the hot water bath to melt the compound until the temperature of the liquid is above 65^{o}C .
5. Remove the test tube from the hot water bath, dry the outside, and place inside the larger, outer test tube attached to the ring stand. Begin constant stirring. The top of the temperature probe should be held during stirring to lift the probe slightly from the bottom of the test tube and to be held straight to prevent scratching on the stirrer. Watch to make sure the tip of the temperature probe remains in the liquid at all times.
6. Start data collection by clicking the green ▶ Collect button on the screen. Continue constant stirring until the freezing point plateau is reached and the temperature begins to decrease.
   - It is very likely that the temperature will drop below the freezing point (supercooling will occur) then rise as the liquid begins to solidify. Then the temperature will plateau (the freezing point). This part of the procedure requires patience.
7. Once the freezing point is evident stop data collection by clicking the red ■ Stop button on the screen.
8. Evaluate both the graph and scroll through the numerical data to identify the freezing point of the pure phenyl salicylate which corresponds to the **highest plateau temperature after supercooling**. Record the freezing point.
9. To save the graph, choose *Experiment* from the top menu then *Store Latest Run*.
10. Follow Clean-up Procedure for Organic Solvent and Solution Waste located on page 8-8 in the Waste Handling and Clean-up portion of the experiment.

II. Determine the freezing point of phenyl salicylate-commercial benzoic acid solution

1. After cleaning in hexanes, reconnect the Temperature Probe to CH1 on the side of the Vernier interface.
2. Repeat the Hardware and Software Initialization procedure found in the page 8-4.
3. Obtain a clean-dry disposable 6” test tube and place in100 mL beaker. Place both on a balance. Tare the balance.
4. Remove the test tube from the beaker and add 5.00 to 5.10 g of phenyl salicylate to the test tube. **Record the mass**. Do not spill the phenyl salicylate. Wash the scoopula with hexanes.
5. **This entire step must be completed at the balance. Bring a disposable weigh dish, cleaned scoopula and data sheet to the balance before beginning.**
   - In a disposable weigh dish mass between 0.20 g to 0.22 g of commercial benzoic acid. Remove weigh dish from the balance. **DO NOT record this mass**.
   - Place the test tube containing phenyl salicylate in a 100 ml beaker and place both on the balance. Tare the balance.
   - Remove the test tube and beaker from the balance. By squeezing the weigh dish at opposite corners to create a funnel tap the dish to transfer the benzoic acid from the weigh dish to the test tube containing the phenyl salicylate (not all will transfer).
   - Place the test tube back into the beaker and place on the balance. **Record the mass of the benzoic acid transferred to the test tube**.
6. Place the temperature probe and wire stirrer into the test tube and melt in the hot water bath until the temperature of the liquid is above 65^{o}C. *If the temperature reading is frozen*, click the green ▶ Collect button then the red ■ Stop button to check the temperature. We will not save the reading so when clicking the collect button once again, choose “*Erase and Continue*” from the dialog box if it appears.
7. Remove the test tube from the hot water bath, dry the outside, and place inside the larger, outer test tube attached to the ring stand. Begin constant stirring.
8. Start data collection by clicking the green ▶ Collect button on the screen. Continue constant stirring until the freezing point plateau is reached and the temperature begins to decrease. Remember to hold the top of the temperature probe during stirring to lift the probe slightly from the bottom of the test tube and to hold straight to minimize scratching on the stirrer. Watch to make sure the tip of the temperature probe remains in the liquid at all times.
   - The freezing point plateau may be much smaller than that of the pure solvent, so be alert.
9. Once the freezing point is evident stop data collection by clicking the red ■ Stop button on the screen.
10. Evaluate both the graph and scroll through the numerical data to identify the freezing point of the pure phenyl salicylate which corresponds to the **highest plateau temperature** after supercooling. Record the freezing point.
11. To save the graph, choose *Experiment* from the top menu then *Store Latest Run*.
12. Follow Clean-up Procedure for Organic Solvent and Solution Waste located on page 8-8 in the Waste Handling and Clean-up portion of the experiment.

III. Determine the freezing point of phenyl salicylate-experimental benzoic acid solution

1. After cleaning in hexanes, reconnect the Temperature Probe to CH1 on the side of the Vernier interface. Repeat the Hardware and Software Initialization procedure found in the page 8-4.
2. Obtain a clean-dry disposable 6” test tube and place in100 mL beaker. Place both on a balance.
3. Tare the balance then into the test tube **mass the same quantity** of phenyl salicylate used to prepare the phenyl salicylate-commercial benzoic acid solution. IT IS IMPORTANT THAT THE GRAMS OF PHENYL SALICYLATE <u>MATCH CLOSELY</u>. Mass carefully as to avoid spilling. **Record the mass**. Wash the scoopula with hexanes.
4. **This entire step must be completed at the balance. Bring your watchglass containing the experimental benzoic acid, cleaned scoopula and data sheet to the balance before beginning.**
   - Place the test tube containing phenyl salicylate in a 100 ml beaker and place both on the balance. Tare (zero) the balance.
   - Remove the test tube and beaker from the balance. Using a scoopula, transfer <u>small quantities</u> of the experimental benzoic acid until the **mass transferred is the same** as the quantity used to prepare the phenyl salicylate-commercial benzoic acid solution. CHECK THE MASS OF BENZOIC ACID FREQUENTLY. IT IS IMPORTANT THAT THE GRAMS OF BENZOIC ACID TRANSFERED <u>MATCH CLOSELY</u>.
   - Place the test tube back into the beaker and place on the balance. **Record the mass of the experimental benzoic acid transferred to the test tube**.
5. Place the temperature probe and wire stirrer into the test tube and melt in the hot water bath until the temperature of the liquid is above 65°C. *Again, if the temperature reading is frozen*, click the green ▶ Collect button then the red ■ Stop button to check the temperature. We will not save the reading so when clicking the collect button once again, choose “*Erase and Continue*” from the dialog box if it appears.
6. Remove the test tube from the hot water bath, dry the outside, and place inside the larger, outer test tube attached to the ring stand. Begin constant stirring. Remember to hold the top of the temperature probe during stirring to lift the probe slightly from the bottom of the test tube and to hold straight to minimize scratching on the stirrer. Watch to make sure the tip of the temperature probe remains in the liquid at all times.
7. Start data collection by clicking the green ▶ Collect button on the screen. Continue constant stirring until the freezing point plateau is reached and the temperature begins to decrease.
   - The freezing point plateau may be small before the temperature drops toward room temperature, so be alert.
8. Once the freezing point is evident stop data collection by clicking the red ■ Stop button on the screen.
9. Evaluate both the graph and scroll through the numerical data to identify the freezing point of the pure phenyl salicylate which corresponds to the **highest plateau temperature** after supercooling. Record the freezing point.
10. Follow Clean-up Procedure for Organic Solvent and Solution Waste located on page 8-8 in the Waste Handling and Clean-up portion of the experiment.

11. Prepare your graph and submit for grading.
    - Add a title to your graph by selecting *Options* from the top menu then *Graph Options* or by right clicking on the graph and selecting *Graph Options*. Select the *Graph Options* tab to type a title in the appropriate box.
    - Choose landscape orientation by selecting *File, Page Setup*
    - Screenshot the graph and send it to your lab partner.
    - Paste the cooling curve screenshot into a Word Document. Orient the page in Word as Landscape and enlarge the plot to fill the entire page.
    - Insert text boxes to label each cooling curve with the name of the solvent and solute (if added).
    - Save the file and submit online for grading.

Waste Handling and Clean Up:

- **Clean –up Procedure for the Organic Solvent and Solution Waste**.
    a. Disconnect the temperature probe from the interface.
    b. With the stirrer and temperature probe still in the test tube, re-melt the organic solvent/solution in the hot water bath.
    c. Take the liquid containing test tube, stirrer, and temperature probe to the waste hood area. Remove the stirrer and temperature probe and place the test tube containing the solution in the rack provided.
    d. Remove any remaining solution from the temperature probe and stirrer by immersing and swishing in the hexane available in the hood. This is an organic solution that is not soluble in water. ***This step is best accomplished <u>before</u> the solution re-solidifies**.
    e. Verify that all organic solute and solvent has been removed from the temperature probe and stirrer through the melting process and final rinse with hexane.
    f. Place used weigh dishes on tray in waste hood.
- Dispose excess benzoic acid in the solid waste disposal container in the waste hood.
- Return all equipment to original location.
- Verify that balance is clean and doors are shut. Brush any spilled organic reagents into a weigh dish and place in the waste hood.
- Wipe down benchtop area, including the sink area, with a damp sponge.

Data Analysis:

Calculate the van't Hoff factor for solutions of benzoic acid-phenyl salicylate

The van't Hoff factor is found by solving for i using K_f (phenyl salicylate) = 10.6 °C·kg/mol. Use the data collected for the solution of phenyl salicylate-commercial benzoic acid solution in these calculations.

1. Determine the difference in the freezing point between the pure phenyl salicylate solvent and the solution of phenyl salicylate and commercial benzoic acid.

$$\Delta T_f = T_{f(\text{pure phenyl salicylate})} - T_{f(\text{phenyl salicylate + commercial benzoic acid})}$$

2. Determine the molality of the solution of phenyl salicylate-commercial benzoic acid. Remember: In this solution benzoic acid is the solute and phenyl salicylate is the solvent.

$$\frac{(\text{mass of commercial benzoic acid, g})/(\text{molar mass of benzoic acid, }\frac{\text{g}}{\text{mol}})}{\text{kg of phenyl salicylate}} = molality, mol/kg$$

3. Calculate the van't Hoff factor (i) for the benzoic acid/phenyl salicylate solution system.

$$i = \frac{\Delta T_f}{K_f(m)}$$

Calculate the Molar Mass of Experimentally Synthesized Benzoic acid

Use the data collected for the solution of phenyl salicylate-experimental benzoic acid solution in these calculations.

1. Determine the difference in the freezing point between the pure phenyl salicylate and the experimentally synthesized benzoic acid/phenyl salicylate solution.

$$\Delta T_f = T_{f(\text{pure phenyl salicylate})} - T_{f(\text{phenyl salicylate + experimental benzoic acid})}$$

2. Determine the molality of the phenyl salicylate-experimental benzoic acid solution. Use the value of i calculated above and K_f (phenyl salicylate)= 10.6 °C·kg/mol.

$$m = \frac{\Delta T_f}{iK_f}$$

3. Calculate the moles of experimental benzoic acid present in the solution from the molality of the solution and the kg of phenyl salicylate present.

$$\left(m, \frac{mol}{kg}\right)(kg\ phenyl\ salicylate) = \ moles\ experimental\ benzoic\ acid$$

4. Determine the molar mass of the experimentally synthesized benzoic acid from the moles of solute and mass of solute used

$$\frac{mass_{experimental\ benzoic\ acid}\ ,g}{moles_{experimental\ benzoic\ acid},mol} = molar\ mass_{\ experimental\ benzoic\ acid}$$

5. Determine the purity of the experimentally synthesized benzoic acid by calculating the percent error in molar mass.

$$\frac{\left|molar\ mass_{experimental\ benzoic\ acid} - molar\ mass_{\ benzoic\ acid}\right|}{molar\ mass_{\ benzoic\ acid}}\ x\ 100\% = \%\ error$$

Data Sheet

Date: ___________ Name:_______________________________________

124L section ___________ Instructor_____________________________________

Partner ______________________________________

I. Freezing point of pure solvent

Freezing point of pure phenyl salicylate __________

II. Freezing point of phenyl salicylate-commercial benzoic acid solution

Mass of phenyl salicylate __________

Mass of commercial benzoic acid **transferred** to phenyl salicylate __________

Freezing point of phenyl salicylate-commercial benzoic acid solution __________

III. Freezing point of phenyl salicylate-experimental benzoic acid solution

Mass of phenyl salicylate __________

Mass of experimental benzoic acid **transferred** to phenyl salicylate __________

Freezing point of phenyl salicylate-experimental benzoic acid solution ___________

Report Sheet Name:____

Date: ___________ Section #/Instructor_____________________________

Calculate the van't Hoff factor, i, for solution of phenyl salicylate-benzoic acid solutions.
Show all work.

ΔT_f	
Molality of the solution	
Van't Hoff factor, i	

Determine the molar mass of the experimentally synthesized benzoic acid compound.
Show all work

ΔT_f	
Molality of the solution	
Moles of experimental benzoic acid	
Experimental molar mass of benzoic acid	

1. Analysis of purity
   a. Calculate percent error in molar mass of the experimentally synthesized benzoic acid and the commercial benzoic acid.

   b. As a measure of purity, comment on the magnitude of difference in molar mass. High purity was achieved if you found a percent error is less than 5% in the above calculation.