EXPERIMENT 16

Determination of Molar Mass by Freezing Point Depression

Objective

Determine the molar mass of an unknown that is a nonelectrolyte and nonvolatile using freezing point depression of a known solvent and the freezing point depression, K_f, from experimental data.

Introduction

When a non-volatile substance is dissolved in a solvent, the vapor pressure of the solvent is lowered. This affects the boiling and freezing temperatures of the solution by lowering the freezing point and elevating the boiling point relative to the pure solvent. Those properties that depend solely on the number of solute particles (ions or molecules) and are nor dependent on the properties of those particles are called **colligative properties**.

Can this freezing point depression or boiling point elevation be put to any practical use? Certainly! In this experiment you will use the freezing point depression to determine the molar mass of an unknown substance. You can also use this phenomena to raise the boiling point of the water that cools your car. It is called **antifreeze**, but in San Diego there is little reason to be concerned about your coolant freezing. Antifreeze depresses the freezing point and elevates the boiling point of the coolant water in your radiator. This is important because as soon as the water in your radiator boils it no longer is useful as a coolant.

Molality, m, is used to express the concentration of the solute. Remember, molality is the number of moles of a solute dissolved in kilograms of solvent.

$$molality = m = \frac{\text{moles of solute}}{\text{kg of solvent}} \qquad \text{(EQ 16.1)}$$

Freezing point depression is found by finding the difference in the freezing point of the pure solvent from that of the solution.

$$\Delta T_f = T^\circ_{f\,\text{pure solvent}} - T^\circ_{f\,\text{solution}} \qquad \text{(EQ 16.2)}$$

The relationship between the freezing point of solution and the freezing point of the pure solvent is:

$$\Delta T_f = K_f m \qquad \text{(EQ 16.3)}$$

It is important to note that this equation is for non-dissociating substances. You need to account for the number of ions in solution for those substances that dissociate. For these compounds the total number of ions must be accounted for.

$$\Delta T_f = i K_f m \qquad \text{(EQ 16.4)}$$

In Equation 16.4, the van't Hoff factor, i, represents the total number of ions produced in solution per formula unit of salt. For example, i for $CaCl_2$ is three; for each formula unit there are three ions present upon dissociation.

EXAMPLE 16.1

Analysis of β-carotene, a dietary source of vitamin A, shows that it contains 10.51% H and 89.49% C. Dissolving 0.0250 g of β-carotene in 1.50 g of camphor gives a freezing point depression of 1.17 °C. What is the molecular weight of β-carotene?

Use Equation 16.3 to solve for the number of molality of solution.

$$m = \frac{\Delta T}{K_f} = \frac{1.17}{37.7} = 0.0310 \frac{\text{mol β-carotene}}{1000 \text{ g camphor}} \qquad \text{(EQ 16.5)}$$

Now, use the calculated molality to determine the number of moles of solute.

$$1.50 \text{ g camphor} \times \frac{0.0310 \text{ mol β-carotene}}{1000 \text{g camphor}} = 4.66 \times 10^{-5} \text{ mol β-carotene} \qquad \text{(EQ 16.6)}$$

Remember, molar mass has units of g/mole. You know the number of moles of solute and the mass of the solute. The molar mass can now be calculated.

$$\frac{0.0250 \text{ g β-carotene}}{4.66 \times 10^{-5} \text{ mol β-carotene}} = 537 \text{g/mole} \qquad \text{(EQ 16.7)}$$

Procedure

Part I: Determining the Freezing Point of Pure Lauric Acid

In order to calculate the molar mass of the unknown solute in Part III, you will need to measure the freezing point of the pure solvent.

1. Weigh a large test tube to the nearest 0.001 g, and add approximately 8 g of lauric acid. Re-weigh the test tube and its contents.

2. Prepare a water bath by filling a 400 mL beaker with tap water and support the beaker on a ring clamp furnished with wire gauze. Heat the beaker of water with a Bunsen burner or hot plate to between 70-80 °C. Make sure that the water level remain above 200 mL in this beaker.

    While the sample is melting prepare the electronic interface to run an experiment collecting the temperature. Sample the temperature about once every two seconds. **Don't forget to calibrate your thermistor**.

3. Fill a second beaker with room temperature tap water on your bench (20-25 °C).

4. Clamp the test tube containing the lauric acid to the ring stand and immerse it in the hot water. After all the lauric acid has been liquefied wait an additional 2-3 minutes. The lauric acid will begin to melt as soon as the water temperature is above its melting point. **Be Cautious! Do not spill hot lauric acid on yourself or touch the bottom of the test tube.**

5. Lower the test tube into the room temperature bath, add a stir bar and the thermistor. **Make sure that the thermistor does not touch or become to close to the stir bar.** Run the thermistor program until the liquid is solid and the stir bar stops moving. Your sample will begin to freeze and the stirrer will no longer spin. Your curve may look something like that illustrated in Figure 16.1. **Make sure that you save your data to a flash drive.**

    FIGURE 16.1
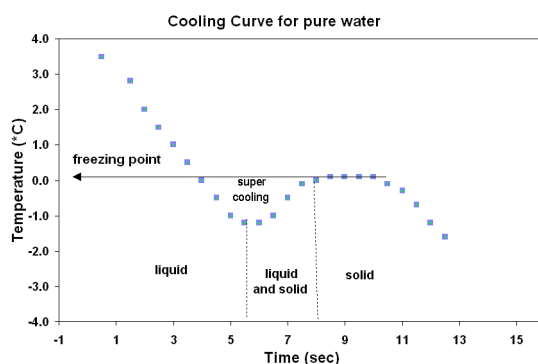
6. **Do not attempt to pull the probe out of the solidified sample (even a little) - this might damage it.** Use the hot water bath to re-melt the acid and gently remove the probe when the sample liquefies. Repeat the experiment a second time.

7. Once finished re-melt the sample and remove the probe. Carefully wipe any excess sample from the probe with a tissue. Clean up any drips or spills in the hood and balance area. Save your data to a flash drive. **Do not put the reagents down the sink! Dispose of chemicals as instructed.**

Part II: Measuring the Freezing point for Lauric Acid/Water Solution

In order to determine K_f for lauric acid, you need to also determine the freezing point for a solution with known concentration. You will use DI water as your known solute.

1. Add 1-2 mL of the DI water to your test tube containing the lauric acid. Re-weigh the test tube and contents.

2. Repeat steps 2-7 in Part I to determine the freezing point of this solution. **Make sure that you save your data to a flash drive**.

Part III: Measuring the Freezing point for Lauric Acid/Unknown Solute Solution

In order to determine the molar mass of the unknown solute, the freezing point of the solution must be determined. In this manner the molar mass can be determined using the value for K_f and ΔT_f. An example of this calculation is found in Example 16.1.

1. Discard the contents of the previous steps in the labeled waste container under the hood. Weigh about 1 gram of an unknown solute to the nearest 0.001 g.

2. Add this to a known amount of lauric acid. Once again, use approximately 8 grams of the solvent weighed to the nearest 0.001 g. Mix the solute and solvent using a mortar and pestle. If the two solids are not well mixed, the unknown acid will form a layer at the bottom of the test tube and will not melt.

3. Repeat steps 2-7 in Part I to determine the freezing point of this solution. **Make sure that you save your data to a flash drive**.

4. Dispose of your solution appropriately and make sure the balance area, reagent area and hoods are clean.

Data Treatment

1. Determine the freezing point for each run using the graphs. Make sure that you use appropriate techniques to account for any supercooling (Your instructor will help you with this). There should be a total of six experimental runs: 2 for the pure solvent, 2 for the known solute (optional), and 2 for the unknown solute. Average the two runs for each determination and use those in subsequent calculations. Compare your freezing point for the pure solvent to that found in the *CRC Handbook*. Calculate a percent error.

2. If Part II was completed, calculate K_f for lauric acid and compare it to the literature value by calculating a percentage error. If Part II was not completed use the literature value of lauric acid ($K_f = 3.90$ °C/*m*) in your molar mass determination.

3. Calculate the molar mass of your unknown solute.

Post Lab Questions

1. A solution is prepared by dissolving 4.9 g sucrose ($C_{12}H_{22}O_{11}$) in 175 g water. Calculate the freezing point of this solution.

2. Is the freezing point of 0.01 m KF $_{(aq)}$ higher or lower than that of 0.01 M glucose $_{(aq)}$? Explain.

3. The freezing point of t-butanol is 25.50 °C and K_f is 9.1 °C/m. Usually t-butanol absorbs water on exposure to air. If the freezing point of a 10.0 g sample of t-butanol is 24.59 °C, how many grams of water are present in the sample?

4. A 0.350 g sample of a large biomolecule was dissolved in 15.0 g of chloroform, and the freezing point depression was determined to be 0.240 °C. Calculate the molar mass of the biomolecule (K_f for chloroform is 4.70 °C/m).

5. In the winter of 1994, record low temperatures were registered throughout the United States. For example, in Champaign, Illinois, a record low of –29 °F was recorded. At this temperature can the salting of icy roads with calcium chloride be effective in melting the ice? Assume that the solubility of calcium chloride in cold water is 74.5 g per 100.0 grams of water.

6. The freezing point depression constants of the solvents cyclohexane and naphthalene are 20.1°C/m and 6.94°C/m respectively. Which would give a more accurate determination by freezing point depression of the molar mass of a substance that is soluble in either solvent? Why?

7. A forensic chemist is given a white solid that is suspected of being pure cocaine ($C_{17}H_{21}NO_4$, molar mass = 303.35 g/mol). She dissolves 1.22 ± 0.01 g of the solid in 15.60 ± 0.01 g benzene. The freezing point is lowered by 1.32 ± 0.04°C.

   a. What is the molar mass of the substance?

   b. Assuming that the percent uncertainty in the calculated molar mass is the percent uncertainty in the temperature change, calculate the uncertainty in the molar mass.

   c. Could the chemist unequivocally state that the substance is cocaine? For example, is the uncertainty small enough to distinguish cocaine from codeine ($C_{18}H_{21}NO_3$, molar mass = 299.36 g/mol)?

   d. Assuming that the absolute uncertainties in the measurements of temperature and mass remain unchanged, how could the chemist improve the precision of her results?