Colligative Properties: Freezing Point Depression and Molecular Weight

Purpose:

The first purpose of this lab is to experimentally determine the van't Hoff (i) factor for two different substances, sucrose ($C_{12}H_{22}O_{11}$) and sodium chloride (NaCl). From the discussion above you should be able to ascertain these values. However, these theoretical values are only valid for very dilute solutions (<0.01 m). At higher concentrations, the ions do not behave independently and so the values of (i) will be less than theoretical. The second purpose of this lab is to determine the molecular weight of commercial antifreeze.

Introduction:

Solutions are homogeneous mixtures that contain two or more substances. The major component is called the *solvent*, and the minor component(s) are called the *solute(s)*. Since the solution is primarily composed of solvent, the physical properties of the solution resemble those of the pure solvent. However, some of these physical properties, called *colligative properties*, are independent of the nature of the solute and depend only upon the concentration of solute particles. Examples of colligative properties include vapor pressure reduction, boiling point elevation, freezing point depression, and osmotic pressure.

Pure water freezes at 0.0 °C (273 K), boils at 100.0 °C (373 K), and exerts a vapor pressure of 23.76 mm Hg at 25.0 °C (298 K). These values are altered by the presence of a solute. You are probably familiar with some common examples of these effects: Antifreeze is used to lower the freezing point and raise the boiling point of your engine coolant (water); and salt is used to melt ice on road.

These effects are expressed quantitatively by the *colligative-property law*, which states that the freezing point and boiling point of a solution differ from those of the pure solvent by amounts that are directly proportional to the *molal* concentration of the solute. In its general form this equation is written:

$$\Delta T = K \cdot m$$

where ΔT is the boiling point elevation or freezing point depression, K is a constant that is specific for each solvent, and m is the molality of the solution and is expressed as the number of moles of solute per kilogram of solvent. Some representative constants, boiling points, and freezing points are given in the table below.

Solvent	Freezing Point, °C	K_{fp},°C	Boiling point,°C	K_{bp},°C
CH_3CO_2H (acetic acid)	16.6	3.90	118.1	2.93
C_6H_6 (benzene)	5.4	5.12	80.2	2.53
$CHCl_3$ (chloroform)	-63.5	4.68	61.3	3.63
C_2H_5OH (ethyl alcohol)	-141		78.4	1.22
H_2O (water)	0.0	1.86	100.0	0.512
$C_{10}H_8$ (naphthalene)	80.6	6.9	218	5.65
C_6H_{12} (cyclohexane)	6.5	20.0	81	2.79
$C_{10}H_{16}O$ (camphor)	179	39.7	208	5.95

The equations relating the boiling point elevation and freezing point depression to molality are:

Colligative Properties: Freezing Point Depression and Molecular Weight

$$\Delta T_{bp} = K_{bp} \cdot m \cdot i$$

$$\Delta T_{fp} = K_{fp} \cdot m \cdot i$$

where ΔT_{bp} and ΔT_{fp} are the change in boiling point and freezing point respectively, K_{bp} and K_{fp} are the boiling and freezing constants for a particular solvent, and i is the van't Hoff factor which is used to account for the number of particles a given solute generates in solution. Substances are usually classified as ionic or covalent, or more precisely, *electrolytes* and *non electrolytes*. Electrolytes dissolve in a solvent to give *ions* (charged particles) in solution while non electrolytes dissolve to give *molecules*. A mole of non electrolyte such as ethanol would dissolve to produce a mole of ethanol molecules. However, a mole of sodium chloride ($NaCl$) would dissolve to form two moles of ions (Na^+ and Cl^-). Because colligative properties are related to the number of solute particles, we would expect a mole of NaCl to have twice the effect as a mole of ethanol. Therefore, (i =1) for ethanol and other non electrolytes, (i =2) for NaCl, and (i = 5) for $Al_2(CO_3)_3$.

EXAMPLE 1

If 10g of ethanol, C_2H_5OH, is dissolved in 100 g of pure water, what would the boiling point and freezing point be for this solution?

First determine the molality of the solution. To do this we need to know the moles of solute and kilograms (Kg) of solvent:

$$(10 \text{ g } C_2H_5OH) \cdot (1 \text{ mole } / 46.069 \text{ g}) = 0.217 \text{ moles}$$

$$\text{molality (m)} = \text{moles ethanol / kg water} = 0.217 \text{ mol} /0.100 \text{ kg} = 2.17 \text{ m}$$

For water the $K_{bp} = 0.52°C/m$, and $K_{fp} = 1.86°C/m$. So for this ethanol solution,

$$\Delta T_{bp} = (0.52°C/m) \cdot (2.17 \text{ m}) \cdot (1) = 1.13°C$$

the boiling point is increased by 1.13°C to 101.13°C. Likewise, the freezing point

$$\Delta T_{fp} = (1.86°C/m) \cdot (2.17 \text{ m}) \cdot (1) = 4.04°C$$

is decreased by 4.04°C to –4.04°C. *It is very important to not confuse the actual freezing point with the freezing point depression!*

EXAMPLE 2

In example one, it was assumed that the van't Hoff factor for ethanol had a value of one (i=1). However, this is only true for very dilute solutions. Assume that the same ethanol/water solution had an experimentally determined freezing point of -3.75°C. We could calculate the van't Hoff factor as follows:

$$\Delta T_{fp} = K_{fp} \cdot m \cdot i$$

$$(i) = \Delta T_{fp} / (K_{fp} \cdot m)$$

$$(i) = 3.75°C / (1.86°C/m \cdot 2.17m)$$

$$(i) = 0.93$$

You can also see that if the molal freezing point depression constant is known, it is possible to calculate the molecular weight of a solute by measuring the freezing point of a solution that contains a known amount of solvent and solute. Lets say you were attempting to determine the molecular weight of urea (CH_4N_2O) using the freezing point depression of naphthalene ($C_{10}H_8$). During the experiment, you found that a solution containing 15 g of urea in 100 g of naphthalene had a freezing point of 63.3°C. From the table above, we see that the freezing point of pure naphthalene is 80.6°C. Therefore, ΔT = 17.3°C. We will also assume, since urea is a non-ionic solid, that i = 1. From the above table, we know that the K_{fp} for naphthalene is 6.9°C/m. Therefore, we can calculate the molality of our solution:

$$\Delta T_{fp} = K_{fp} \cdot m \cdot i$$

$$17.3°C = 6.9°C/m \cdot m \cdot 1$$

$$m = 2.51$$

Remember that molality is defined as the number of moles of solute per 1000 g of solvent. However, in this example, we only used 100 g of solvent (naphthalene), and so the moles of urea are:

$$(2.51 \text{ moles/kg}) \cdot (0.1 \text{ kg}) = 0.251 \text{ moles of urea}$$

Since moles can be calculated by dividing the grams of a substance by the molecular weight of that substance, we can now calculate the molecular weight of urea:

$$\text{moles} = \text{grams / mol. wt.}$$

$$\text{mol. wt.} = \text{grams / moles}$$

$$\text{mol. wt.} = 15 \text{ g} / 0.251 \text{ moles}$$

Thus the molecular weight of urea is 59.8 g/mol.

Method:

In this experiment you will need to determine the freezing point depression for several solutions. However, the temperature at which a solution freezes is difficult to determine by direct visual observation because of a phenomenon called super cooling and also because solidification of solutions usually occurs over a broad temperature range. To overcome these problems, temperature-time graphs, called *cooling curves*, are used which readily reveal the true freezing temperature. The major features of a general cooling curve are shown below:

Colligative Properties: Freezing Point Depression and Molecular Weight
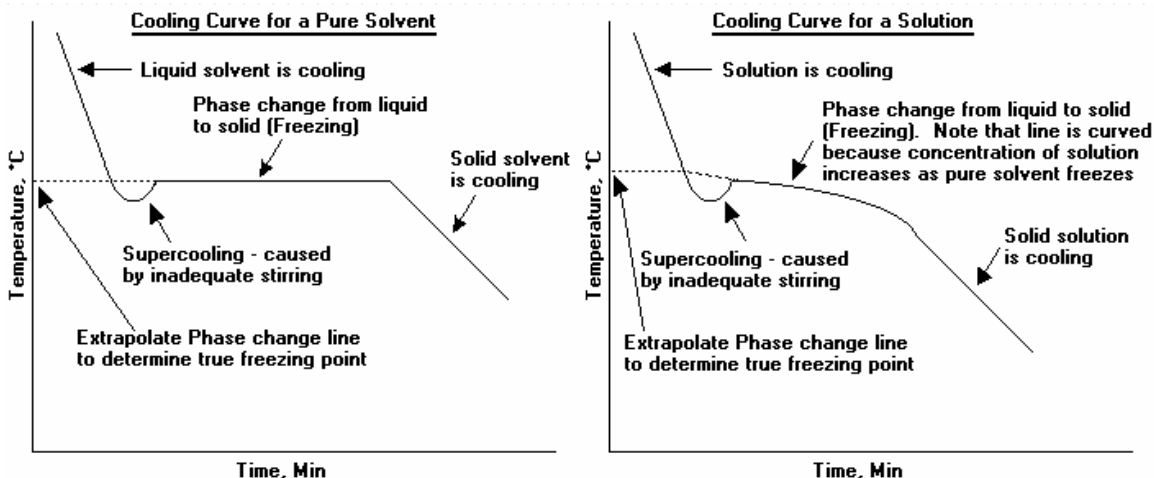
You will construct cooling curves for both the pure solvent (water) and various solutions. From the cooling curve you will extrapolate the true freezing temperature. Extrapolation is necessary because as the solution freezes the solid that is formed is essentially pure solvent. The remaining solution becomes more and more concentrated and its freezing point becomes lower and lower. Also, super cooling introduces an ambiguity in the freezing point and should be minimized using through stirring.

Materials:

- Large Styrofoam cup
- Distilled water
- $NaCl_{(s)}$
- Thermometer
- Glass stirring rod

- Antifreeze (Ethylene Glycerol may be substituted)
- Test Tube
- Sucrose
- Ice

Procedure:

Preparation of an Ice Bath:

1. Fill a large Styrofoam cup with ice.
2. Add approximately 150 mL of distilled water to the cup.
3. Add approximately 25 g of salt to the cup.
4. Stir this ice-salt mixture with your glass stirring rod until a temperature range of -5 °C to -10 °C is obtained.

    Note: colder temperatures are easily obtained by adding more salt, however, it makes the solutions cool too fast to obtain good results.

5. Be sure to check the temperature of the ice bath BEFORE each experiment. If the temperature of the bath rises above -5 °C, then drain the water and add more ice and salt.

Colligative Properties: Freezing Point Depression and Molecular Weight

Molecular Mass Determination from Freezing Point Depression:

1. Dissolve approximately 3.1 g of commercial antifreeze in 50 g of water (weigh both accurately). Mix until both liquids have completely dissolved.
2. Be sure to use a clean and dry the test tube and add approximately 15 ml of the solution previously prepared.
3. Place the test tube, thermometer and agitator into the ice bath so that the level of the water in the test tube is below the level of the ice. Make sure you can still read the thermometer.
4. **Record** the temperature of the antifreeze solution every **30 seconds** while vigorously agitating.
5. Continue to record the temperature until the solution solidifies.

   Note: these solutions tend to form a slush which makes it difficult to observe the exact freezing point. **Keep collecting data until you obtain 5 - 10 readings below the freezing point of water.**

6. Remove the test tube and put the contents in the marked antifreeze waste bottle. You will need to rinse, and dry the test tube between trails.
7. Repeat the cooling curve a second time.

   Note: Dispose of any left over antifreeze solution in the marked antifreeze waste bottle in the hood.

Determination of (i) for Sucrose:

1. Prepare a solution of sucrose by adding approximately 17 g of sucrose ($C_{12}H_{22}O_{11}$) to 50 g of water (weigh both accurately). Mix until all crystals have dissolved.
2. Be sure your large test tube is clean and dry and add approximately 15 ml of the sucrose solution to it.
3. Place the test tube, thermometer and agitator into the ice bath so that the level of the water in the test tube is below the level of the ice. Make sure you can still read the thermometer.
4. **Record** the temperature of the sucrose solution every **30 seconds** while vigorously agitating.
5. Continue to record the temperature until the solution solidifies.

   Note: these solutions tend to form a slush which makes it difficult to observe the exact freezing point. Keep collecting data until you obtain 5 - 10 readings below the freezing point of water.

6. Remove the test tube and dump the contents down the drain. You will need to rinse, and dry the test tube between trails.
7. Repeat the cooling curve a second time.

Colligative Properties: Freezing Point Depression and Molecular Weight

Determination of (i) for NaCl:

1. Prepare a solution of NaCl by adding approximately 2.9 g of table salt to 50 g of water (weigh both accurately). Mix until all crystals have dissolved.
2. Be sure to use a clean and dry the test tube and add approximately 15 ml of the sodium chloride solution to it.
3. Place the test tube, thermometer and agitator into the ice bath so that the level of the water in the test tube is below the level of the ice. Make sure you can still read the thermometer.
4. **Record** the temperature of the saline solution every **30 seconds** while vigorously agitating.
5. Continue to record the temperature until the solution solidifies.

   Note: these solutions tend to form a slush which makes it difficult to observe the exact freezing point. Keep collecting data until you obtain 5 - 10 readings below the freezing point of water.

6. Remove the test tube and dump the contents down the drain. You will need to rinse, and dry the test tube between trails.
7. Repeat the cooling curve a second time.

Cooling Curve for Pure Water:

1. Be sure to use a clean and dry the test tube and add approximately 15 ml of distilled water to it.
2. Place the test tube, thermometer and agitator into the ice bath so that the level of the water in the test tube is below the level of the ice. Make sure you can still read the thermometer. You need the agitator to keep ice from forming on the edges of the test tube.
3. **Record** the temperature of the water every **30 seconds** while vigorously agitating.
4. Continue to record the temperature until the water solidifies.

   Note: it is difficult to determine the freezing point of pure water. Keep collecting data until you have at least 5 reading at the same temperature.

5. Remove the test tube and dump the ice down the drain. You will need to rinse and dry the test tube between trails.
6. Repeat the cooling curve a second time.

Colligative Properties: Freezing Point Depression and Molecular Weight

DATA:

Antifreeze					Sucrose			
Mass of Antifreeze:					Mass of Sucrose:			
Mass of Water:					Mass of Water:			
#	Time	1ST Trial Temp (°C)	2nd Trial Temp (°C)		#	Time	1ST Trial Temp (°C)	2nd Trial Temp (°C)
1	0:00				1	0:00		
2	0:30				2	0:30		
3	1:00				3	1:00		
4	1:30				4	1:30		
5	2:00				5	2:00		
6	2:30				6	2:30		
7	3:00				7	3:00		
8	3:30				8	3:30		
9	4:00				9	4:00		
10	4:30				10	4:30		
11	5:00				11	5:00		
12	5:30				12	5:30		
13	6:00				13	6:00		
14	6:30				14	6:30		
15	7:00				15	7:00		
16	7:30				16	7:30		
17	8:00				17	8:00		
18	8:30				18	8:30		
19	9:00				19	9:00		
20	9:30				20	9:30		
21	10:00				21	10:00		
22	10:30				22	10:30		
23	11:00				23	11:00		
24	11:30				24	11:30		
25	12:00				25	12:00		
26	12:30				26	12:30		
27	13:00				27	13:00		
28	13:30				28	13:30		
29	14:00				29	14:00		
30	14:30				30	14:30		
31	15:00				31	15:00		

Colligative Properties: Freezing Point Depression and Molecular Weight

#	Time	NaCl 1ST Trial Temp (°C)	NaCl 2nd Trial Temp (°C)
	Mass of NaCl:		
	Mass of Water:		
1	0:00		
2	0:30		
3	1:00		
4	1:30		
5	2:00		
6	2:30		
7	3:00		
8	3:30		
9	4:00		
10	4:30		
11	5:00		
12	5:30		
13	6:00		
14	6:30		
15	7:00		
16	7:30		
17	8:00		
18	8:30		
19	9:00		
20	9:30		
21	10:00		
22	10:30		
23	11:00		
24	11:30		
25	12:00		
26	12:30		
27	13:00		
28	13:30		
29	14:00		
30	14:30		
31	15:00		

#	Time	Pure Water 1ST Trial Temp (°C)	Pure Water 2nd Trial Temp (°C)
1	0:00		
2	0:30		
3	1:00		
4	1:30		
5	2:00		
6	2:30		
7	3:00		
8	3:30		
9	4:00		
10	4:30		
11	5:00		
12	5:30		
13	6:00		
14	6:30		
15	7:00		
16	7:30		
17	8:00		
18	8:30		
19	9:00		
20	9:30		
21	10:00		
22	10:30		
23	11:00		
24	11:30		
25	12:00		
26	12:30		
27	13:00		
28	13:30		
29	14:00		
30	14:30		
31	15:00		

Colligative Properties: Freezing Point Depression and Molecular Weight

Calculations:

From your cooling curves, calculate:

- The freezing point of pure water _____
- The freezing point of the sucrose solution _____
- The freezing point of the sodium chloride solution _____
- The freezing point of the antifreeze solution _____

From your freezing points, calculate:

- The effective (i) for the sucrose solution _____
- The effective (i) for the sodium chloride solution _____
- The molecular weight of the antifreeze _____

Questions:

- Report the average (i) value obtained for the sucrose solution

  _____

- Report the average (i) value obtained for the sodium chloride solution

  _____

- Report the average molecular weight for the commercial antifreeze

  _____

- What values of (i) did you expect for sucrose and sodium chloride?

  _____
  - Did your experiment confirm this? _____
  - Why or why not? _____
- What was the effect of more or less stirring on the super cooling portion of the cooling curve?

  _____
  _____